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NEWFIELDS

DRAFT REPORT

ENVIRONMENTAL FORENSIC INVESTIGATION
GOWANUS CANAL
BROOKLYN, NEW YORK

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prepared for

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Executive Summary

This report presents the results of an environmental forensic investigation of hydrocarbons and PAHs in the Gowanus Canal in Brooklyn, New York. It compared the hydrocarbon fingerprints of samples from accessible source area to sediment samples collected from the Gowanus Canal. The source samples included tar from the former Citizens MGP, tar from the former Witco/Barrett tar products facility, some regional pavement, and adjacent subsurface soils. This investigation produced the following conclusions:

- Many landside sources of hydrocarbons and PAHs exist around the Gowanus Canal. Sediment impacts were observed from the following landside source materials: middle distillate diesel and fuel oil, abraded pavement, tars near the former Witco and Barrett facilities, and tar from the former Citizens MGP. Other PAH sources are likely, but presently unidentified.

- The shallow sediments from 0 to 3 feet below the bottom of the canal (bbc) were generally deposited after 1950 and contained predominantly petroleum products mixed with combustion or tar derived PAHs. Lower concentrations were generally observed in these surface sediments than in deeper sediments.

- The deeper sediments below 3 feet bbc contained accumulated and native sediments deposited before 1950. These deeper sediments contained high PAH concentrations dominated by tar and lesser amounts of petroleum. The native sediments contained the highest concentrations of PAHs.

- The PAH signature of tars resembling the former Citizens MGP plant were observed in a limited number of sediment samples. Most of the samples containing tar derived PAHs did not resemble source samples from the Citizens Site. This finding suggested the significant role of multiple PAH sources in the Gowanus Canal.

- An allocation model demonstrated the relative amounts of petroleum and tar in each forensic sample. This model revealed the dominant presence of petroleum in shallow sediments and tar in deeper sediments. Mixtures of petroleum and tar were evident in surface sediments along a contiguous stretch of the Middle and Lower Reaches where the surficial sediments appear scoured away. The sediment scouring was attributed to barge traffic.

In summary, the Gowanus Canal sediments contain a complex mixture of hydrocarbons from many sources. Petroleum products dominated the shallow sediments and tars dominated the deeper sediments.

1. OBJECTIVE

Gowanus Canal is an engineered drainage system in the southern region of Brooklyn, New York. The sediments in the Gowanus Canal contain environmental contaminants including complex mixtures of hydrocarbons. A class of hydrocarbons known as polycyclic aromatic hydrocarbons (PAHs) have many sources; for example, industry, vehicular emissions, building materials, abraded roadway pavement, petroleum products, and soot. Former manufactured gas plants (MGPs) generated a byproduct, known as tar, which also contains PAHs. Other industrial sources of tar include tar product manufacturers that produced roadway pavement, roofing shingles, housing insulation, paints, weatherproofing, and many more. Residues of these many historical building products can be found in industrial, commercial, and residential areas. Over time, these residues wash into the Gowanus Canal through storm drains and other pathways. This environmental investigation was designed to survey and identify the likely origins of hydrocarbons and PAHs in the Gowanus Canal sediments. The field operations were performed by GEI Consultants, Inc. (GEI) under contract with KeySpan Corporation.

2. TECHNICAL APPROACH

The Gowanus Canal was geographically divided into three sections for this study (Figure 1). The Upper Reach extended south from the Flushing Tunnel to the junction with the 4th Street Turning Basin. The Middle Reach extended from the junction with the 4th Street Turning Basin to the Gowanus Expressway. The Lower Reach extended from the Gowanus Expressway to the Upper New York Bay.

The sediment core logs recognized three general geological layers. The depth intervals are described in this report as the depth below the bottom of the canal (bbc). The deepest stratum consisted of native material that preceded human development of the area. The native stratum was generally deep (> 10 feet bbc) in the Upper and Lower Reaches and shallow (< 10 feet bbc) in the Middle Reach. The shallow sediments were functionally defined as the top 3 feet bbc. The remaining accumulated sediments were between 3 feet bbc and the native material.

The identification of hydrocarbon and PAH sources in the Gowanus Canal was based on a comprehensive sampling program conducted by KeySpan and GEI Consultants, Inc. (GEI). One hundred and twenty-four samples were collected for forensic analyses from the Gowanus Canal study area (Table 1). An overview of these samples follows.

2.1 Sediment Core Samples

The sediment sampling program involved the collection of samples along 28 transects throughout the Gowanus Canal (Figure 1). Transects A to I were in the Upper Reach, Transects J to V were in the Middle Reach, and Transects W to AA were in the Lower Reach. Each transect was oriented perpendicular to the flow of water and consisted of three sediment sampling locations spaced approximately equally between the shorelines. Inter-transect sediment cores were collected in the Middle Reach of the Gowanus Canal to increase the sampling resolution between the Railway Bridge and the junction with the 4th Street Turning Basin. One to three additional sediment sampling locations were also positioned in the 4th Street, 6th Street, 7th Street, and 11th Street Turning Basins. Sediment core samples were collected by Vibracore technique to approximately 20 feet bbc (or refusal). Samples from three depth intervals (typically, one from the surface, accumulated, and native geological horizons) were collected from each core for priority pollutant analytes. One sample from each core was submitted for forensic hydrocarbon analysis.

2.2 Dated Sediment Cores

Six of the sediment cores were collected in duplicate such that the second core could be used for radionuclide analyses (Figure 1). This core was sliced into 2 cm intervals from the top of the sediment core to a depth of 150 cm bcc. Deeper core intervals were sliced in 10 cm intervals. Lead-210 (Pb-210) and cesium-137 (Cs-137) were analyzed in selected sediment sample intervals to estimate the sedimentation and accumulation rates for each dated sediment core.

2.3 Soil Borings

Subsurface soil samples were collected on the shoreline of the Gowanus Canal to demonstrate the types of hydrocarbons likely migrating into the canal. Soil borings were collected near the shoreline on either side of the Gowanus Canal transects with a Geoprobe. A subsurface soil sample was collected from the depth of maximum hydrocarbon concentration. It was not possible to collect many of the planned soil borings due to property access limitations.

2.4 Pavement Samples

Six pavement samples were collected to partially identify the types of roadway material used around the Gowanus Canal. The pavement samples were collected for forensic analysis when the soil boring was collected below a paved roadway. Two additional pavement samples were collected to the east and west of the Citizens Former MGP location on the northwestern side of the Middle Reach. The pavement samples were collected using a Geoprobe.

2.5 Tar Samples

Two tar samples were collected from monitoring wells (MW7I and MW8I) on the former Citizens Gas Plant along the northwestern side of the Middle Reach. These samples were recovered from the intermediate depth monitoring wells with a disposable bailer. These samples presumably represented tars generated or processed at the Citizens plant. These subsurface NAPL samples were spatially diverse and considered representative of tars released from the facility over a long period of time.

One tar bleb was collected near Transect A (RH039) by skimming the surface of the water with a wide mouth jar. This sample was collected at the outlet of a storm sewer and possibly representative of an unidentified NAPL release.

2.6 Seep Samples

Eight seep samples were collected in the Red Hook neighborhood to the west of the Lower Reach. These tar samples were collected near the former Barrett and Witco tar products manufacturing facilities with a stainless steel knife. These seeps were attributed to industrial wastes from the Barrett and Witco operations. They represented a range of tar wastes from these sites, but the full range of chemical signatures present at depth was not comprehensively studied.

3. ANALYTICAL METHODS

The samples were prepared and analyzed in accordance with published methods (Emsbo-Mattingly *et al.*, 2003; Stout *et al.*, 2003; Stout *et al.*, 2002). The samples were analyzed by several methods in order to provide a detailed description of hydrocarbons with a broad molecular weight range. In general, the high resolution hydrocarbons fingerprint painted a broad-brush picture of the dominant extractable hydrocarbons types while the mass spectrophotometric methods provided more detailed and purified profiles of the tar and petroleum (Emsbo-Mattingly *et al*., 2003; Stout *et al*., 2002). Six sediment cores were analyzed for Pb-210 and Cs-137 to determine the sedimentation and accumulation rates. Collectively, these data were used to characterize the types of hydrocarbon materials in the study samples.

3.1 Sample Collection and Shipping

The field team collected 124 field samples between December 14, 2005 and September 6, 2006 from the Gowanus Canal Study Area. Table 1 summarizes the field sample identifications, abbreviations, collection dates, and matrices. The samples were shipped via overnight courier and received in good condition at or below 6°C.

Several sample identities required clarification. Sample GC-SED-16 (0-2) was misidentified on the chain of custody (COC) as GC-SED-16 (14.5-15.5). Sample GC-SED-102 (6.5-8.5) was reported on the COC, but not delivered to the laboratory. Sample GC-SED-71C (1.5-2.5) was received by the laboratory, but not recorded on the COC. Sample GC-SED-RH 039 was misidentified as GC-SED-RM 039. All of these corrections were confirmed by GEI.

Specific information related to chain of custody and sample receipt was provided in Attachment G.

3.2 Hydrocarbon Sample Preparation

An aliquot of each solid sample (30 g wet weight) was fortified with surrogates, dried with sodium sulfate and serially shake extracted with dichloromethane (DCM). Less sample was used when high concentrations of extractable organic matter was present. The sample extracts were concentrated by Kuderna-Danish and nitrogen blow down techniques. Sulfur and polar interferences were removed with a copper powder and alumina, respectively. The non-aqueous phase liquid (NAPL) forensic reference materials (crude oil, kerosene, and diesel) were diluted to approximately 5 mg/ml in DCM. The sample extracts and diluents were split prior to analysis. The extracts were fortified with internal standards and submitted for GC/FID and GC/MS/SIM analyses (described below).

3.3 High Resolution Hydrocarbon Fingerprint and TPH

The sample extracts were analyzed using a high-resolution gas chromatograph equipped with a flame ionization detector (GC/FID). High resolution GC/FID fingerprints were generated over a broad carbon range (approximately n-C_9 to n-C_{40}) that provided an overall assessment of the non-volatile hydrocarbons present in each sample. These fingerprints provided information on the dominant extractable hydrocarbons that might include pyrogenic PAHs, petroleum products, and detrital vegetation. The total concentration of these hydrocarbons was measured as total petroleum hydrocarbons (TPH). The GC/FID fingerprints for each field and QC sample were placed in Attachment C.

3.4 Polycyclic Aromatic Hydrocarbons (PAH)

The sample extracts were also analyzed using a high-resolution gas chromatograph equipped with a mass spectrometer operated in the selected ion monitoring mode (GC/MS/SIM). The instrument was calibrated to allow for quantification of a broad range of 2- through 6-ring PAH, selected alkylated PAH homologues, selected sulfur-containing compounds (dibenzothiophenes), and other compounds useful for the identification of hydrocarbon sources in the environment. Table 2 presented an inventory of the target compounds along with abbreviations used in selected figures of this report. The PAH sample

concentrations are summarized in Attachment D. The full laboratory reports with quality control results are included in Attachment G.

The acronym EPAPAH is used in the discussion in reference to the sum of the 16 individual EPA Priority Pollutant PAH compounds (EPAPAHs). These compounds do not contain alkyl functional groups (a.k.a., parent PAHs). The parent PAHs are more abundant in combustion or tar derived products. The concentrations of these target compounds helped qualitatively and quantitatively compare the candidate source and Gowanus Canal sediment samples. The concentrations of PAHs in soil and sediment samples were reported in dry weight units.

3.5 Saturated Hydrocarbon Fingerprints and Triterpane Biomarkers

Environmental forensic investigators demonstrated that the presence and/or pattern of biomarkers reveal information about the specific source(s) of petrogenic residues in the environment; e.g., petroleum or coal (Stout *et al*., 2002). An aliquot of the GC/FID extract was solvent exchanged and fractionated on silica gel to remove the aromatic hydrocarbons that can interfere with the analyses of saturated hydrocarbons and biomarkers. This purified extract was injected into a GC/MS/SIM instrument. Saturated hydrocarbon fingerprints were generated from this analysis (Attachment E). These fingerprints helped identify the types of petroleum products in the sample and possibly the feedstock from which the tar was generated. In addition, the laboratory generated triterpane biomarker fingerprints (Attachment F). The relative abundances diagnostic biomarkers helped identify different types of petroleum and coal.

3.6 Radionuclide Analyses

Lead-210 (Pb-210) was used to calculate a site-specific sedimentation rate based on its measured activity and constant rate of decay. Excess Pb-210 produced in the atmosphere migrates to the earth's surface though precipitation and decays with a half-life of 22.3 years. The decay process results in an exponential decrease in Pb-210 activity with depth that can be used to estimate sediment age back about 100-150 years (Donnelly and Bertness 2001; Lavelle *et al.*, 1985; Lavelle *et al.*, 1986). A nominal 3 g aliquot of sediment sample was dried, digested in acid, and plated onto a small metal disk. Polonium-208 (P0-208) was added as an internal standard. The radioactive emissions of P0-208 and Po-210 were counted using an alpha particle spectrometer for approximately 24 hours per sample. The results were calculated and reported in disintegrations per minute per gram (dpm/g). The Pb-210 activity for unmeasured depth intervals was averaged using the section activity directly above and directly below the sampling interval.

The Cs-137 data were used to independently evaluate the sedimentation rate calculated using the Pb-210 data. This technique is based on historical release of Cs-137, which is a radioactive isotope by-product of nuclear weapons testing. Measurable concentrations of this isotope first appeared in the atmosphere in about 1952, peaked during 1963-64, and declined thereafter (Juracek *et al.*, 1998). Cs-137 maxima in sediments corresponded to approximately 1960 ± 5 years. Each sample was analyzed directly for radioactive emissions of Cs-137 with a gamma counter for approximately 12 to 24 hours per sample. The results were calculated and reported in disintegrations per minute per gram (dpm/g). The maximum amount of Cs-137 was attributed to the year 1960 $\pm$ 5 years.

The full laboratory report and associated QC results are included in Attachment H.

3.7 Visual Presentation of Data

This investigation generated a substantial quantity of chemistry data, both chromatographic and numerical. In order to present this data in a meaningful manner, we used a variety of visual and graphical techniques to display and explain the most significant features. Largely, we relied upon four methods of data visualization in this report. These include:

- Gas Chromatograms presented the raw output from analytical instruments used to characterize the hydrocarbon distributions.

- Scatter Plots depicted the two dimensional relationship between two hydrocarbon parameters in a format amenable to establishing qualitative trends or quantitative correlations.

Whenever possible, color coding and symbols were used to illustrate the most relevant compositional features.

4. RESULTS AND DISCUSSION

We divided the results and discussion into method-specific sections for ease of presentation. It opens with a discussion of the major hydrocarbon patterns evident in the GC/FID data. Thereafter, we present a more detailed description of the tar and petroleum materials evident in the GC/MS/SIM data. These data helped equate source identification features in the absence of compounds that might otherwise interfere with the interpretation. Herein, the PAH data proved most useful for differentiating tar in the source samples from tar in the sediment while the saturated hydrocarbons and biomarkers helped describe the petroleum materials. Finally, we concluded this section with a spatial integration of the hydrocarbon signatures discussed previously. In essence, the last section summarized the findings in horizontal, vertical, and, to a limited extent, temporal dimensions. The high resolution hydrocarbon fingerprints, PAH results, saturated hydrocarbon fingerprints, triterpane biomarker fingerprints, and radionuclide results are included in Attachments C to H.

4.1 Dominant Hydrocarbon Signatures

High resolution hydrocarbon fingerprints (GC/FID) revealed the dominant hydrocarbon patterns in the environmental samples. The principal patterns of interest in the sediment samples included urban runoff with localized influences of low level middle distillate and tar products (e.g., creosote, paving tar, and others). This section describes the identification of these hydrocarbon materials based on characteristic assemblages of saturated and aromatic hydrocarbons eluting between n-nonane (n-C_9) and n-tetratriacontane (n-C_{40}) in the high resolution hydrocarbon fingerprints.

The discussion of the dominant hydrocarbon signatures is organized spatially using representative transects in the Upper, Middle, and Lower Reaches of the Gowanus Canal. The figures include a map with sample locations using the sample key from Figure 1; for example, sediment samples are green circles, product samples are yellow triangles, etc…. The high resolution hydrocarbon fingerprints of the transect samples depict the dominant hydrocarbon types. Major petroleum constituents are highlighted in red. Major tar and combustion constituents are highlighted in blue. Selected PAHs are marked with brown triangles. Large quality control compounds are marked with a circle. Other miscellaneous features are highlighted with a green line. Tar is typically present when naphthalene (N0) or phenanthrene (P0) is the dominant PAH. Weathered tar, pitch, or soot may be present when pyrene (PY0), chrysene (C0), or benzo(a)pyrene (BAP) are the dominant PAH.

Three sediment samples were collected from Transect A (Figure 2a). GC-SED-01 (19-20') was collected in the native sediment layer. It primarily contained tar as indicated by high levels of N0 and P0 with little or no petroleum. GC-SED-02 (17.1-18.1') was also collected in the native sediment layer. It contained tar (dominant N0 and P0) with some middle range petroleum. GC-SED-03 (0-1.5') was collected from a shallow sediment layer. It primarily contained heavy range petroleum as indicated by the broad late eluting unresolved complex mixture (UCM). The PAHs may indicate the presence of whether tar or combustion byproduct. A tar bleb (RH039) was collected near a storm sewer outfall at the end of Douglas Street. It consisted of lightly weathered tar.

Three sediment samples were collected from Transect B (Figure 2b). GC-SED-07 (7.5-8.5') was collected in the accumulated sediment layer. It primarily contained middle and heavy petroleum was indicated by the broad UCM. It also contained low levels of PAHs likely derived from weathered tar and soot. Several unidentified, late eluting peaks were possibly attributed to sewage. GC-SED-08 (10.5-11.5') was collected in the native sediment layer. It primarily contained lightly weathered tar has indicated by the PAH profile dominated by N0. GC-SED-09 (6-7') was collected in the accumulated sediment layer. It contained a mixture of lightly weathered tar and petroleum. The subsurface soil below the western side of the Canal represented by GC-GP-05 (33-35') contained lightly weathered tar. The subsurface soil below the eastern side of the Canal (near the former Fulton MGP) represented by GC-GP-06 (17-17.1') contained middle distillate petroleum indicated by resolved hydrocarbons and UCM eluting between approximately *n*-decane (*n*-C_{10}) and *n*-hexacosane (*n*-C_{26}). The high levels of isoprenoids hydrocarbons

relative to normal alkanes indicated heavy biodegradation. This petroleum distillate was consistent with weathered heating fuel oil.

The three sediment samples collected from Transect D (Figure 2c) contained petroleum with lower levels of PAHs likely derived from and soot. The surface sediment samples, GC-SED-10 (0-1.5') and GC-SED-11 (1-3') contained heavy petroleum as indicated by the late eluting UCM. The sediment sample from the accumulated sediment layer, GC-SED-12 (13-14'), contained more middle range than heavy range petroleum. A soil boring was also collected on the western side of the Canal. The pavement sample collected at this location, GC-GP-07 (0-0.1'), consisted of heavy residual range petroleum hydrocarbons evidenced by the late eluting UCM. Low levels of middle range heating oil are also present. The subsurface soil at this location, GC-GP-07 (2-3'), contains biodegraded middle range heating oil.

Three sediment samples were collected from Transect F (Figure 2d). GC-SED-16 (0-2') and GC-SED-17 (0-2') were surface sediments that contained a broad, late eluting UCM consistent with abraded pavement and low levels of middle range heating fuel oil. Low levels of PAHs likely derived from tar and soot were also present. GC-SED-18 (7-8') was collected from the native sediment layer. It contained lightly weathered tar.

Three sediment samples were collected from Transect G (Figure 2e). They primarily contained heavy residual petroleum indicated by the broad late eluting UCM. Lower and variable levels of middle range petroleum are also evident in the profile of the UCM in the middle distillate range (UCM contour above the first two PAH triangles representing N0 and P0). Low levels of PAHs at likely associated with soot or weathered tar. A soil boring was collected near the western side of Transect G below 1st Street. The pavement at this location, GC-GP-13, consisted of a heavy late eluting UCM. The homologous series of normal alkanes (resolved peaks on top of the UCM) indicated either fresh pavement or sequestered petroleum residuals. The subsurface soil collected below the pavement, GC-GP-13 (6-8'), contained middle and heavy range fuel oils indicated by the bimodal UCM (two humps). The low abundances of normal alkanes relative to isoprenoids hydrocarbons indicated heavy biodegradation.

The three sediment samples from Transect H (Figure 2f) were collected from the native sediment layer. They contained petroleum with lower levels of PAHs likely derived from tar and soot. The surface sediment samples, GC-SED-10 (0-1.5') and GC-SED-11 (1-3') contained heavy petroleum as indicated by the late eluting UCM. The sediment sample from the accumulated sediment layer, GC-SED-12 (13-14'), contained more middle range than heavy range petroleum. A soil boring was also collected on the western side of the Canal. The pavement sample collected at this location, GC-GP-07 (0-0.1'), consisted of heavy residual range petroleum hydrocarbons evidenced by the late eluting UCM. Low levels of middle range heating oil are also present. The subsurface soil at this location, GC-GP-07 (2-3'), contains biodegraded middle range heating oil.

Three sediment samples were collected from Transect O (Figure 2g). Samples GC-SED-43 (7.3-8.3'). GC-SED-44 (5.6-6.1'), and GC-SED-45 (1-1.5') were collected in the accumulated and surface sediments. They each contained a mixture of tar and petroleum. Like other samples collected in the 6th Street Turning Basin, sample GC-SED-90 (6.5-7') was collected from the native sediment layer and exhibited a mixture of tar and petroleum. Sample CGMW-07I was a product sample collected from a monitoring well associated with former Citizens MGP. The high levels of PAHs, especially N0, indicated the presence of lightly weathered tar. No significant petroleum was observed in this fingerprint.

Three sediment samples were collected from Transect R (Figure 2h). Like Transect O, the surface and accumulated sediments contained a mixture of tar and petroleum. The surface sediment in the 7th Street Turning Basin, GC-SED-93 (0-1') contained a broad late eluting UCM indicative of middle to heavy range petroleum. Pronounced isoprenoids indicated heavy biodegradation. This material was possibly a heavy fuel, crude oil, or heavy residual petroleum (e.g., asphalt) mixed with middle petroleum distillate (e.g., heating fuel oil). Sample GCMW-08I was a product sample collected from a monitoring well associated with former Citizens MGP. The high levels of PAHs, especially N0, indicated the presence of lightly weathered tar. No significant petroleum was observed in this fingerprint.

Two sediment samples were collected for forensic analysis from Transect U (Figure 2i). GC-SED-62 (3-4') was collected from the accumulated sediment layer. It contained lightly weathered tar with lesser amounts of petroleum. GC-SED-63 (3-3.5') contained more petroleum than tar. Sample GC-SED-94 (19-20') was collected from the native sediments within the neighboring 11th St Turning Basin. It contained lightly weathered tar.

Three sediment samples were collected from Transect V and two sediment samples from Transect BB (Figure 2j). The shallow depth to native sediment in this region indicated a high degree of scouring attributed to barge traffic. Samples GC-SED-64 (2-4'), GC-SED-65 (0.5-1.25'). GC-SED-65 (11.5-12.5'), and GC-SED-105 (2.5-4') contained mixtures of lightly weathered tar and petroleum. Sample GC-SED-104 (3.7-5.1') was predominantly petroleum with low levels of PAHs possibly derived from soot. This signature may indicate the presence of a proximal storm sewer outfall conveying roadway runoff or sewage.

Three sediment samples were collected from Transect Y (Figure 2k). All of the samples contained middle and heavy range petroleum attributed to roadway runoff (e.g., abraded pavement and fuel oils). The more surficial sediment sample, GC-SED-75 (0-0.7'), contained higher proportions of petroleum relative to tar or combustion byproducts than the deeper sediments, GC-SED-73 (3.8-4.8) and GC-SED-74 (5.3-6.3').

Five sediment samples were collected from Transect AA (Figure 2l). The hydrocarbons in all of these sediment samples were predominantly derived from petroleum. Like Transect Y, the surface sediments contained higher proportions of middle and heavy UCM relative to the PAHs indicating higher proportions of petroleum relative to tar and combustion byproducts in these samples. The origin of these petroleum products could have been roadway runoff or petroleum storage operations. A PAH profile dominated by N0 was observed in GC-SED-79 (2.5-3.5'), GC-SED-81 (8-11'), and GC-SED-82 (12-12.8), which indicated the presence of lightly weathered tar in these accumulated sediment layer samples.

Eight seep samples were scraped from selected the roadways of Red Hook proximal to the former tar product manufacturing facilities operated by Witco and Barrett (Figure 2m). The hydrocarbon fingerprint of these product samples was consistent with moderately weathered tar dominated by P0. Variability in the relative abundances of FL0 and PY0 (circles) indicated a high degree of variability among these samples. This variability indicates the presence of multiple tar releases in this area.

In summary, the Gowanus Canal sediments exhibited higher proportions of petroleum in the surface sediments (0 to 3 feet bbc) relative to tar and combustion byproducts. Pavement samples from several Brooklyn streets closely resembled the heavy range hydrocarbons observed throughout the shallow sediments in the Canal. Subsurface soils collected next to the Canal contained middle distillate diesel or heating fuel oil similar to the middle distillate range petroleum observed in the Canal sediments. The native material contained higher proportions of tar than surface sediments with one general exception. Some samples in the Middle Reach exhibited higher proportions of tar in the surface and accumulated zones likely caused by scouring. Although not comprehensively investigated, several tar sources were identified near the Gowanus Canal. These sources included the former Citizens MGP, Witco, and Barrett facilities. The specific origin of the tar residues in the Canal is discussed further in the discussion of PAH source signatures below.

4.2 Dates of Sediment Deposition

The dated sediment cores helped contextualize the general changes in hydrocarbon composition with depth (Table 3). A dated core was collected from Transect A in at sampling location GC-SED-01. Three samples were collected from a paired core for PAHs measured by EPA 8270C (STL) and one split sample of native material from the 19 to 20 foot bbc interval was submitted for forensic analysis (NF). The concentration of benzo(a)pyrene (BAP) was similar in the split samples, which demonstrated that the results were generally comparable between the two laboratories. More importantly, the vertical profile of

BAP indicates low levels of tar and combustion byproducts at the surface with increasing BAP abundances with closer proximity to the native sediment zone.

The radionuclide analysis determined that the sediment in the surface sample collected between 1 and 2.5 feet bbc was deposited between 1989 and 1998. The sediment in the accumulated zone sample (16 to 17 feet bbc) was deposited around 1925 and the sediment in the native material sample (19 to 20 feet bbc) was deposited around 1894. The sedimentation rate of 5.90 g/cm^2/yr and accumulation rate of 4.92 cm/yr were high for intertidal coastlines and likely reflect the flux of particulates through local storm drains and combined sewer overflows (CSOs).

Other dated cores resemble these general trends. For example, the surface sediments (0 to 3 feet) in each core were deposited in the last 25 to 50 years. In many locations (GC-SED-01, GC-SED-12, GC-SED-88, and GC-SED-31), the BAP concentrations are lower in the surface interval than at depth. This indicates that the more modern input of PAHs is lower than in the past. As discussed previously in the discussion of dominant hydrocarbon signatures, the surface sediments predominantly contained middle and heavy range petroleum while the deeper native sediments contained tar (Figure 3). This trend was not clearly observed in GC-SED-21 because sediments from the native interval were not collected due to refusal at 8 feet bbc. This trend was also not observed at GC-SED-87 because 1) the modern deposition of PAHs was high at this location and 2) tar may not have reached native material in this more extreme southeasterly area.

4.3 PAH Source Signatures

The concentration and distribution of polycyclic aromatic hydrocarbons (PAHs) provided greater detail and specificity about the type of petroleum, tar, and urban background in the field samples. At the outset, some basic terminology must be clarified. Petroleum possesses a petrogenic PAH pattern consisting of low parent PAH abundance relative to the alkylated PAHs; e.g., C0 < C1 < C2. By contrast, pyrogenic PAHs form during the partial combustion or pyrolysis of organic matter. A pyrogenic PAH pattern exhibits high abundance of parent PAHs relative to the alkylated PAHs; e.g., C0 > C1 > C2, before weathering. Finally, diagenetic PAHs, like retene and perylene, form naturally in sediments containing specific types of decayed vegetation.

Forensic scientists study the distribution and relative abundances of diagnostic PAH assemblages to help identify the presence of PAHs from these various sources (Stout *et al.*, 2004; Emsbo-Mattingly *et al.*, 2003; Stout *et al.*, 2003; Emsbo-Mattingly *et al.*, 2003; Stout *et al.*, 2002). The reader should bear in mind that that these quantitative PAH concentrations are more reliable source indicators than the peak heights used in the simpler hydrocarbon fingerprinting due, in part, to the potential presence of interferences (e.g., unknown oxygenated hydrocarbons, QC compounds, phthalates, halogenated organics, and others) and subtle chromatographic changes (peak widening) that can occur in the GC/FID fingerprints. Consequently, we used the more reliable PAH data for our definitive source characterization.

As evident in the discussion of dominant hydrocarbon signatures (Section 4.1), most field samples exhibited a PAH pattern dominated by priority pollutant PAHs. These patterns are pyrogenic. They are principally derived from tar and soot. Although petrogenic PAHs are present, this study was focused on recognizing the potential contribution of tar from the former Citizens MGP on Gowanus Canal sediments. This objective was addressed by employing diagnostic PAH ratios that maintain a reasonable degree of source specific character for lightly, moderately, and heavily weathered pyrogenic PAHs (Emsbo-Mattingly *et al.*, 2003). Specifically, the PAH ratios FL0/PY0 and (BBF+BKF)/BAP were calculated for the purpose of resolving the source specific differences among the pyrogenic PAHs in the field samples (Table 4). In addition to being stable when weathered in the environment (Emsbo-Mattingly *et al.*, 2006), these ratios exhibited a high degree of precision (relative percent difference or RPD) among field samples (Table 4, 0% to 17% RPD among duplicates).

A double ratio plot of FL0/PY0 verses (BBF+BKF)/BAP separated the field samples according to the pyrogenic PAHs in each sample (Figure 4a). Samples with petroleum tar signatures grouped in the

center of the plot (0.6 < FL0/PY0 < 0.9 and 0.9 < (BBF+BKF)/BAP < 1.3). Petroleum tars are byproducts generated during the manufacture of gas at carbureted water gas or oil gas plants. Although not favored as a wood preservative, petroleum tar was used to bind roadway pavement and preserve a wide range of historical building materials. Samples plotting to the lower left (FL0/PY0 < 0.6 and (BBF+BKF)/BAP < 0.9) contain middle petroleum distillates typically from diesel or heating fuel oils. Samples plotting in the upper left (FL0/PY0 < 0.7 and (BBF+BKF)/BAP > 1.2) contained heavy petroleum from bunker fuels and abraded pavement. Samples plotting in the upper right (FL0/PY0 > 0.9 and (BBF+BKF)/BAP > 1.2) contain coal tar products including many forms of creosote and building materials. In summary, this plot reveals that most of the PAHs in the Gowanus Canal were derived from petroleum tar. The samples from the former Citizens MGP plot among these sediment samples.

The 95% (error bars) and 99% (box) confidence intervals were calculated for the samples collected from the former Citizens MGP (Figure 4b). These results revealed a narrow compositional signature for the Citizens MGP tars. A small number of sediments from the Upper and Middle Reaches fell into the compositional range of the Citizens MGP tars (Figure 4c). Most of these sediments were collected in the native sediment layer (Figure 4d), none were observed in the accumulated sediments (Figure 4e), and a few were observed in the surface sediments (Figure 4f). In summary, the impact of tar from the former Citizens MGP was limited. The wide range of petroleum tar residues in the Gowanus Canal sediments was largely attributed to unidentified tar and combustion byproduct sources.

4.4 Petroleum and Tar Mixing Model

A mixing model was developed for estimating the percentage of petroleum and tar in each sample. The model was based on the relative abundances of total priority pollutant EPAPAHs (Tables 2 and 4) and TPH (Table 4). The EPAPAHs comprise the dominant pyrogenic PAHs in tar. The TPH concentration is the sum of all hydrocarbons (e.g., petroleum and tar) eluting between *n*-nonane (*n*-C_9) and *n*-tetratriacontane (*n*-C_{40}). Therefore, the ratio of EPAPAHs/TPH will be high when tar is dominant and low when petroleum is dominant. The precision of this ratio among replicates (Table 4) was good for estimating the relative abundance of tar and petroleum (RPD from 1% to 25%).

The mixing model was based on the average EPAPAH/TPH ratio among the tar samples from the former Citizens MGP and heavy petroleum in the pavement samples. The percentage of tar in each sample was calculated using the formula:

$$\%Tar = \frac{Rs - Rp}{Rt - Rp} \times 100$$

where,
Rs = Ratio of EPAPAH/TPH for the sample,
Rp = Average Ratio of EPAPAH/TPH for the pavement (0.0002796), and
Rt = Average Ratio of EPAPAH/TPH for the tar (0.2610).

Any percentages of tar greater than 100% were set to 100%. The percentage of petroleum was calculated as the difference between 100% and the percentage of tar. The sample specific results for this allocation were presented on Table 4. Based on inspection of the fingerprinting data, the precision of this method is on the order of $\pm$ 10%.

The significance of this allocation model was evident when the allocation was simplified into three categories. These categories were: “Petroleum” when they contain more than 75% petroleum, “Tar” when they contain more than 75% tar, and “Mixture” when they contain between 25% and 75% petroleum and tar. When normalized to the boundary between the accumulated and native sediments (Figure 5a), the allocation demonstrated that the native sediments in the Upper, Middle, and Lower Reaches contained tar or tar and tar-petroleum mixtures. By contrast, the accumulated sediments contained

petroleum and tar-petroleum mixtures. When the cores were normalized to the depth of the bottom of the Canal (Figure 5b), the prevalence of petroleum in the surface sediments was clear throughout much of the Upper, Middle, and Lower Reaches. The exposure of native sediments from Transect M through Y reflected the mobilization or mixing of tar residues into the surface sediments. The tar impacted sediments would likely be buried below at least 3 feet of sediment containing predominantly petroleum impacts from non-MGP sources (e.g., roadway runoff) if scouring did not occur in this region of the Gowanus Canal.

5. SUMMARY

This report presents the results of an environmental forensic study of hydrocarbons and PAHs in the Gowanus Canal in Brooklyn, New York. This investigation was intended to assist the KeySpan project team form a conceptual site model for the Gowanus Canal study area. The technical approach for this investigation involved the collection of sediments from multiple strata within the Gowanus Canal in additional to accessible source area samples. The source samples included tar from the former Citizens MGP, tar from the former Witco/Barrett tar products facility, some regional pavement, and adjacent subsurface soils. Advanced chemical analyses were performed on the field samples. These results generated the following conclusions:

- Many landside sources of hydrocarbons and PAHs exist around the Gowanus Canal. The following landside source materials were consistent with the chemistry of sediments from the Gowanus Canal: middle distillate diesel and fuel oil, abraded pavement, tars near the former Witco and Barrett facilities, and tar from the former Citizens MGP. Other PAH sources are likely, but presently unidentified.

- The shallow sediments from 0 to 3 feet below the bottom of the canal (bbc) were generally deposited after 1950 and contained predominantly petroleum products mixed with combustion or tar derived PAHs. Lower concentrations were generally observed in these surface sediments than in deeper sediments.

- The deeper sediments below 3 feet bbc contained accumulated and native sediments deposited before 1950. These deeper sediments contained high PAH concentrations dominated by tar and lesser amounts of petroleum. The native sediments contained the highest concentrations of PAHs.

- The PAH signature of tars resembling the former Citizens MGP plant were observed in a limited number of sediment samples. Most of the samples containing tar derived PAHs did not resemble source samples from the Citizens Site. This finding suggested the significant role of multiple PAH sources in the Gowanus Canal.

- An allocation model demonstrated the relative amounts of petroleum and tar in each forensic sample. This model revealed the dominant presence of petroleum in shallow sediments and tar in deeper sediments. Most sediment samples contained PAHs from mixed petroleum, tar, and combustion sources, especially in the Middle Reach where surficial sediments appear scoured away. The sediment scouring was attributed to barge traffic.

In summary, the Gowanus Canal sediments contain a complex mixture of hydrocarbons from many sources. Petroleum products dominated the shallow sediments and tars dominated the deeper sediments.

6. REFERENCES

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Attachment A
Tables

Table 1. Field Samples

Sample ID	Forensic Sample Abbrev.	Location		Average Sample Depth (feet)	Depth to Native Material (feet)	Lab ID	Matrix	Date Collected	Date Received	High Resolution Hydrocarbon Fingerprint	Quantitative PAHs	Saturated Hydrocarbons & Biomarkers
GC-SED-01 (19-20)	01	Upper Reach	Transect A	19.5	17.2	0512110-13	Sediment	12/19/2005	12/20/2005	X	X	X
GC-SED-02 (17.1-18.1)	02	Upper Reach	Transect A	17.6	10.6	0512110-14	Sediment	12/19/2005	12/20/2005	X	X	X
GC-SED-03 (0-1.5)	03	Upper Reach	Transect A	0.75	9.3	0512110-12	Sediment	12/19/2005	12/20/2005	X	X	X
GC-SED-RH 039	RH039	Upper Reach	Storm Sewer	0	NA	0512128-05	Product	12/23/2005	12/28/2005	X	X	X
GC-SED-04 (10.3-11.3)	04	Upper Reach	Transect B	10.8	11.3	0512128-04	Sediment	12/23/2005	12/28/2005	X	X	X
GC-SED-05 (0-2) *	05	Upper Reach	Transect B	1	13	0512128-03	Sediment	12/23/2005	12/28/2005	X	X	X
GC-SED-07 (7.5-8.5) *	07	Upper Reach	Transect C	8	11	0512110-11	Sediment	12/19/2005	12/20/2005	X	X	X
GC-SED-08 (10.5-11.5)	08	Upper Reach	Transect C	11	10.5	0512128-01	Sediment	12/23/2005	12/28/2005	X	X	X
GC-SED-09 (6-7)	09	Upper Reach	Transect C	6.5	15.2	0512128-02	Sediment	12/23/2005	12/28/2005	X	X	X
GC-SED-10 (0-1.5) *	10	Upper Reach	Transect D	0.75	10.4	0512124-04	Sediment	12/21/2005	12/23/2005	X	X	X
GC-SED-11 (1-3)	11	Upper Reach	Transect D	2	13	0601019-01	Sediment	1/5/2006	1/10/2006	X	X	X
GC-SED-12 (13-14)	12	Upper Reach	Transect D	13.5	14.2	0512124-03	Sediment	12/21/2005	12/23/2005	X	X	X
GC-SED-13B (14.6-15.6)	13	Upper Reach	Transect E	15.1	9.4	0601019-05	Sediment	1/7/2006	1/10/2006	X	X	X
GC-SED-14 (5.5-6.5)	14	Upper Reach	Transect E	6	5.9	0601019-04	Sediment	1/7/2006	1/10/2006	X	X	X
GC-SED-15 (0-0.75) *	15	Upper Reach	Transect E	0.375	7.1	0601019-03	Sediment	1/7/2006	1/10/2006	X	X	X
GC-SED-16 (0-2)	16	Upper Reach	Transect F	1	5.3	0601019-08	Sediment	1/8/2006	1/10/2006	X	X	X
GC-SED-17 (0-2)	17	Upper Reach	Transect F	1	5	0601019-07	Sediment	1/8/2006	1/10/2006	X	X	X
GC-SED-18 (7-8)	18	Upper Reach	Transect F	7.5	4.7	0601019-02	Sediment	1/7/2006	1/10/2006	X	X	X
GC-SED-19C (1.5-2)	19	Upper Reach	Transect G	1.75	6.8	0601019-11	Sediment	1/9/2006	1/10/2006	X	X	X
GC-SED-20 (4-5)	20	Upper Reach	Transect G	4.5	5	0601040-03	Sediment	1/10/2006	1/12/2006	X	X	X
GC-SED-21B (7-8)	21	Upper Reach	Transect G	7.5	8	0601019-10	Sediment	1/9/2006	1/10/2006	X	X	X
GC-SED-22B (19.3-20)	22	Upper Reach	Transect H	19.65	8	0601019-09	Sediment	1/9/2006	1/10/2006	X	X	X
GC-SED-23 (17.5-19)	23	Upper Reach	Transect H	18.25	5.5	0601040-02	Sediment	1/10/2006	1/12/2006	X	X	X
GC-SED-24 (12.6-13.4)	24	Upper Reach	Transect H	13	6.8	0601040-01	Sediment	1/10/2006	1/12/2006	X	X	X
GC-SED-25 (9-10)	25	Upper Reach	Transect I	9.5	5	0601045-01	Sediment	1/12/2006	1/17/2006	X	X	X
GC-SED-26 (5.3-5.8)	26	Upper Reach	Transect I	5.55	3.25	0601045-06	Sediment	1/12/2006	1/17/2006	X	X	X
GC-SED-27 (4.9-5.4)	27	Upper Reach	Transect I	5.15	8	0601045-05	Sediment	1/12/2006	1/17/2006	X	X	X
GC-SED-28 (4.9-5.8)	28	Middle Reach	Transect J	5.35	8.8	0601045-04	Sediment	1/12/2006	1/17/2006	X	X	X
GC-SED-29 (7.4-8.4)	29	Middle Reach	Transect J	7.9	4.6	0601045-03	Sediment	1/12/2006	1/17/2006	X	X	X
GC-SED-30 (3.5-5.5)	30	Middle Reach	Transect J	4.5	5.3	0601045-02	Sediment	1/12/2006	1/17/2006	X	X	X
GC-SED-31 (2.5-4.5)	31	Middle Reach	Transect K	3.5	12.5	0601050-02	Sediment	1/16/2006	1/18/2006	X	X	X
GC-SED-32 (5.9-6.9)	32	Middle Reach	Transect K	6.4	6.9	0601050-01	Sediment	1/16/2006	1/18/2006	X	X	X
GC-SED-33 (1.5-3) *	33	Middle Reach	Transect K	2.25	10.2	0601050-06	Sediment	1/17/2006	1/18/2006	X	X	X
GC-SED-34B (2-3) *	34	Middle Reach	Transect L	2.5	6.8	0601045-08	Sediment	1/13/2006	1/17/2006	X	X	X
GC-SED-35 (15.3-17.3)	35	Middle Reach	Transect L	16.3	10.8	0601045-07	Sediment	1/13/2006	1/17/2006	X	X	X
GC-SED-36 (2.5-4.5)	36	Middle Reach	Transect L	3.5	10.25	0601050-03	Sediment	1/16/2006	1/18/2006	X	X	X
GC-SED-37B (7-8)	37	Middle Reach	Transect M	7.5	8	0512124-07	Sediment	12/22/2005	12/23/2005	X	X	X
GC-SED-38 (5.1-6.1)	38	Middle Reach	Transect M	5.6	6.1	0512124-06	Sediment	12/22/2005	12/23/2005	X	X	X
GC-SED-39 (4.5-5.5)	39	Middle Reach	Transect M	5	8.5	0601019-06	Sediment	1/8/2006	1/10/2006	X	X	X
GC-SED-40 (5-6)	40	Middle Reach	Transect N	5.5	0	0601050-05	Sediment	1/17/2006	1/18/2006	X	X	X
GC-SED-41 (7.3-8.3)	41	Middle Reach	Transect N	7.8	0	0601050-04	Sediment	1/17/2006	1/18/2006	X	X	X
GC-SED-43 (7.3-8.3)	43	Middle Reach	Transect O	7.8	8.3	0601064-10	Sediment	1/23/2006	1/24/2006	X	X	X
GC-SED-44 (5.6-6.1)	44	Middle Reach	Transect O	5.85	6.1	0601064-11	Sediment	1/23/2006	1/24/2006	X	X	X
GC-SED-45C (1-1.5)	45	Middle Reach	Transect O	1.25	1.8	0601070-02	Sediment	1/23/2006	1/26/2006	X	X	X
GC-SED-46C (5-5.5)	46	Middle Reach	Transect P	5.25	6.6	0601070-01	Sediment	1/23/2006	1/26/2006	X	X	X
GC-SED-47 (1.5-2.5)	47	Middle Reach	Transect P	2	2.5	0601070-04	Sediment	1/24/2006	1/26/2006	X	X	X
GC-SED-48 (5-5.8)	48	Middle Reach	Transect P	5.4	5.8	0601070-06	Sediment	1/24/2006	1/26/2006	X	X	X
GC-SED-49 (10-11)	49	Middle Reach	Transect Q	10.5	5.9	0601070-05	Sediment	1/24/2006	1/26/2006	X	X	X
GC-SED-50 (2-5)	50	Middle Reach	Transect Q	3.5	5	0601073-01	Sediment	1/26/2006	1/27/2006	X	X	X

Table 1. Field Samples (continued).

Sample ID	Forensic Sample Abbrev.	Location	Average Sample Depth (feet)	Depth to Native Material (feet)	Lab ID	Matrix	Date Collected	Date Received	High Resolution Hydrocarbon Fingerprint	Quantitative PAHs	Saturated Hydrocarbons & Biomarkers
GC-SED-51 (0-1.5) *	51	Middle Reach Transect Q	0.75	7.2	0601073-04	Sediment	1/26/2006	1/27/2006	X	X	X
GC-SED-52 (3-6)	52	Middle Reach Transect R	4.5	6	0601064-03	Sediment	1/20/2006	1/24/2006	X	X	X
GC-SED-53 (0.5-1.5)	53	Middle Reach Transect R	1	2.2	0601064-02	Sediment	1/20/2006	1/24/2006	X	X	X
GC-SED-54B (4.5-5.7)	54	Middle Reach Transect R	5.1	6.6	0601064-01	Sediment	1/20/2006	1/24/2006	X	X	X
GC-SED-55 (1.5-2.5)	55	Middle Reach Transect S	2	10.5	0601070-03	Sediment	1/24/2006	1/26/2006	X	X	X
GC-SED-56 (5.8-6.2)	56	Middle Reach Transect S	6	0	0601073-02	Sediment	1/26/2006	1/27/2006	X	X	X
GC-SED-57 (7-9)	57	Middle Reach Transect S	8	9.5	0601073-03	Sediment	1/26/2006	1/27/2006	X	X	X
GC-SED-58C (8-10)	58	Middle Reach Transect T	9	5	0602004-02	Sediment	1/27/2006	2/1/2006	X	X	X
GC-SED-59 (6-7.25)	59	Middle Reach Transect T	6.625	0	0601064-08	Sediment	1/22/2006	1/24/2006	X	X	X
GC-SED-60B (6.8-8) *	60	Middle Reach Transect T	7.4	6.8	0601064-05	Sediment	1/21/2006	1/24/2006	X	X	X
GC-SED-62C (3-4)	62	Middle Reach Transect U	3.5	9.5	0601064-04	Sediment	1/21/2006	1/24/2006	X	X	X
GC-SED-63 (3-3.5)	63	Middle Reach Transect U	3.25	4.3	0512124-02	Sediment	12/20/2005	12/23/2005	X	X	X
GC-SED-64D (2-4)	64	Middle Reach Transect V	3	0.5	0601040-05	Sediment	1/11/2006	1/12/2006	X	X	X
GC-SED-65 (0.5-1.25)	65	Middle Reach Transect V	0.875	0	0601064-07	Sediment	1/22/2006	1/24/2006	X	X	X
GC-SED-66 (11.5-12.5)	66	Middle Reach Transect V	12	0	0512124-01	Sediment	12/20/2005	12/23/2005	X	X	X
GC-SED-67 (8-8.4)	67	Lower Reach Transect W	8.2	8	0512110-04	Sediment	12/17/2005	12/20/2005	X	X	X
GC-SED-68 (2.2-3.1)	68	Lower Reach Transect W	2.65	2.7	0512110-05	Sediment	12/17/2005	12/20/2005	X	X	X
GC-SED-69 (6-7)	69	Lower Reach Transect W	6.5	9.5	0512110-09	Sediment	12/18/2005	12/20/2005	X	X	X
GC-SED-70B (4-5)	70	Lower Reach Transect X	4.5	0	0602004-10	Sediment	1/29/2006	2/1/2006	X	X	X
GC-SED-71C (1.5-2.5)	71	Lower Reach Transect X	2	7.8	0602004-14	Sediment	1/29/2006	2/1/2006	X	X	X
GC-SED-72 (13.5-14.5)	72	Lower Reach Transect X	14	10	0512110-10	Sediment	12/18/2005	12/20/2005	X	X	X
GC-SED-73E (3.8-8.4) *	73	Lower Reach Transect Y	6.1	3.8	0602004-09	Sediment	1/29/2006	2/1/2006	X	X	X
GC-SED-74 (5.3-6.3)	74	Lower Reach Transect Y	5.8	8.5	0602004-08	Sediment	1/29/2006	2/1/2006	X	X	X
GC-SED-75C (0-0.7) *	75	Lower Reach Transect Y	0.35	0.7	0601070-09	Sediment	1/25/2006	1/26/2006	X	X	X
GC-SED-76C (2.5-3.4)	76	Lower Reach Transect Z	2.95	3.4	0601070-08	Sediment	1/25/2006	1/26/2006	X	X	X
GC-SED-77 (14.5-15.4)	77	Lower Reach Transect Z	14.95	13.6	0602004-13	Sediment	1/30/2006	2/1/2006	X	X	X
GC-SED-78B (2.5-5)	78	Lower Reach Transect Z	3.75	5.8	0601070-07	Sediment	1/25/2006	1/26/2006	X	X	X
GC-SED-79 (2.5-3.5)	79	Lower Reach Transect AA	3	5	0512110-07	Sediment	12/17/2005	12/20/2005	X	X	X
GC-SED-80 (0-2)	80	Lower Reach Transect AA	1	11.8	0512110-06	Sediment	12/17/2005	12/20/2005	X	X	X
GC-SED-81 (8-11)	81	Lower Reach Transect AA	9.5	13.3	0512110-08	Sediment	12/18/2005	12/20/2005	X	X	X
GC-SED-82 (12-12.8)	82	Lower Reach Transect AA	12.4	13.2	0602004-12	Sediment	1/30/2006	2/1/2006	X	X	X
GC-SED-83 (0-2)	83	Lower Reach Transect AA	1	11.9	0602004-11	Sediment	1/30/2006	2/1/2006	X	X	X
GC-SED-84 (6-7)	84	4th Street Turning Basin	6.5	2.8	0512105-07	Sediment	12/15/2005	12/16/2005	X	X	X
GC-SED-85B (8.5-9.3)	85	4th Street Turning Basin	8.9	9.3	0512110-03	Sediment	12/16/2005	12/20/2005	X	X	X
GC-SED-86 (0-1)	86	4th Street Turning Basin	0.5	7.8	0512105-06	Sediment	12/15/2005	12/16/2005	X	X	X
GC-SED-87 (4.4-6.2) *	87	4th Street Turning Basin	5.3	11.8	0512105-08	Sediment	12/15/2005	12/16/2005	X	X	X
GC-SED-88 (15.9-16.9)	88	6th Street Turning Basin	16.4	9.9	0512105-03	Sediment	12/14/2005	12/16/2005	X	X	X
GC-SED-89 (12.8-13.8)	89	6th Street Turning Basin	13.3	7.6	0512105-02	Sediment	12/14/2005	12/16/2005	X	X	X
GC-SED-90B (6.5-7)	90	6th Street Turning Basin	6.75	4.5	0512105-01	Sediment	12/14/2005	12/16/2005	X	X	X
GC-SED-91 (10.2-11.2)	91	7th Street Turning Basin	10.7	10.2	0601064-06	Sediment	1/22/2006	1/24/2006	X	X	X
GC-SED-92 (0-2)	92	7th Street Turning Basin	1	6.8	0512110-02	Sediment	12/16/2005	12/20/2005	X	X	X
GC-SED-93 (0-1)	93	7th Street Turning Basin	0.5	7.8	0512110-01	Sediment	12/16/2005	12/20/2005	X	X	X
GC-SED-94 (19-20)	94	11th Street Turning Basin	19.5	5	0512124-08	Sediment	12/22/2005	12/23/2005	X	X	X
GC-SED-95 (3.5-4.5)	95	Middle Reach Between I&J	4	4.5	0512105-05	Sediment	12/15/2005	12/16/2005	X	X	X
GC-SED-96 (14-15)	96	Middle Reach Between J&K	14.5	11	0512105-04	Sediment	12/15/2005	12/16/2005	X	X	X
GC-SED-97 (8.5-9.5)	97	Middle Reach Between K&L	9	10.5	0602004-07	Sediment	1/28/2006	2/1/2006	X	X	X
GC-SED-98 (1-2)	98	Middle Reach Between L&M	1.5	10.5	0602004-01	Sediment	1/27/2006	2/1/2006	X	X	X
GC-SED-99 (3.5-4.5)	99	Middle Reach Between M&N	4	8.3	0512124-05	Sediment	12/22/2005	12/23/2005	X	X	X
GC-SED-100 (5-6)	100	Middle Reach Between N&O	5.5	7.6	0602004-06	Sediment	1/28/2006	2/1/2006	X	X	X
GC-SED-101 (7.9-9.1)	101	Middle Reach Between P&Q	8.5	7.1	0602004-05	Sediment	1/28/2006	2/1/2006	X	X	X

Table 1. Field Samples (continued).

Sample ID	Forensic Sample Abbrev.	Location	Average Sample Depth (feet)	Depth to Native Material (feet)	Lab ID	Matrix	Date Collected	Date Received	High Resolution Hydrocarbon Fingerprint	Quantitative PAHs	Saturated Hydrocarbons & Biomarkers
GC-SED-102 (2-4) *	102	Middle Reach Between Q&R	3	8.5	0602004-04	Sediment	1/28/2006	2/1/2006	X	X	X
GC-SED-103 (8.1-9.1)	103	Middle Reach Between R&S	8.6	11	0602004-03	Sediment	1/28/2006	2/1/2006	X	X	X
GC-SED-104 (3.7-5.1) *	104	Middle Reach Transect BB	4.4	0	0601040-04	Sediment	1/11/2006	1/12/2006	X	X	X
GC-SED-105 (2.5-4)	105	Middle Reach Transect BB	3.25	0	0601064-09	Sediment	1/22/2006	1/24/2006	X	X	X
GC-GP-06 (0-0.1)	GP06p	Upper Reach Near C (East)	0.05	0	0606091-11	Pavement	6/20/2006	6/21/2006	X	X	X
GC-GP-07 (0-0.1)	GP07p	Upper Reach Near D (West)	0.05	0	0606091-08	Pavement	6/20/2006	6/21/2006	X	X	X
GC-GP-13 (0-0.1) *	GP13p	Upper Reach Near G (West)	0.05	0	0606091-09	Pavement	6/20/2006	6/21/2006	X	X	X
GC-GP-15 (0-0.1)	GP15p	Upper Reach Near H (West)	0.05	0	0606091-10	Pavement	6/20/2006	6/21/2006	X	X	X
CGSB-54B (0-0.25)	SB54B	Middle Reach Luquer St	0.125	0	0606091-06	Pavement	6/20/2006	6/21/2006	X	X	X
CGSB-57 (0-0.1)	SB57	Middle Reach Hoyt St	0.05	0	0606091-07	Pavement	6/20/2006	6/21/2006	X	X	X
GC-GP-05 (33-35)	GP05s	Upper Reach Near C (West)	34	0	0606091-04	Soil	6/14/2006	6/16/2006	X	X	X
GC-GP-06 (17-17.1)	GP06s	Upper Reach Near C (East)	17.05	0	0606091-05	Soil	6/16/2006	6/21/2006	X	X	X
GC-GP-07 (2-3)	GP07s	Upper Reach Near D (West)	2.5	0	0606091-03	Soil	6/13/2006	6/14/2006	X	X	X
GC-GP-13 (6-8)	GP13s	Upper Reach Near G (West)	7	0	0606091-01	Soil	6/12/2006	6/14/2006	X	X	X
GC-GP-15 (9-9.5)	GP15s	Upper Reach Near H (West)	9.25	0	0606091-02	Soil	6/12/2006	6/14/2006	X	X	X
CGMW-07I *	MW07I	Middle Reach Citizens MGP	NA	NA	0602017-01	Product	1/31/2006	2/7/2006	X	X	X
CGMW-08I	MW08I	Middle Reach Citizens MGP	NA	NA	0602017-02	Product	1/31/2006	2/7/2006	X	X	X
FS-Court St Row-1	CSR1	Red Hook Surface Seep	0	NA	0609032-07	Seep	9/6/2006	9/8/2006	X	X	X
FS-Halleck St Row *	HSR	Red Hook Surface Seep	0	NA	0607098-01	Seep	7/19/2006	7/21/2006	X	X	X
FS-Halleck St Row-2	HSR2	Red Hook Surface Seep	0	NA	0609032-05	Seep	9/6/2006	9/8/2006	X	X	X
FS-Halleck St Row-3	HSR3	Red Hook Surface Seep	0	NA	0609032-06	Seep	9/6/2006	9/8/2006	X	X	X
FS-Red Hook-1 *	RH1	Red Hook Surface Seep	0	NA	0609032-01	Seep	9/6/2006	9/8/2006	X	X	X
FS-Red Hook-2	RH2	Red Hook Surface Seep	0	NA	0609032-02	Seep	9/6/2006	9/8/2006	X	X	X
FS-Red Hook-3	RH3	Red Hook Surface Seep	0	NA	0609032-03	Seep	9/6/2006	9/8/2006	X	X	X
FS-Red Hook-4	RH4	Red Hook Surface Seep	0	NA	0609032-04	Seep	9/6/2006	9/8/2006	X	X	X
Total									**124**	**124**	**124**

* Samples run in duplicate

Table 2. Primary PAH Analytes

Analytes	Abbrev	Class	PAH Categories			
			Total	EPA	Sulfur	
			TPAH	EPAPAH	SPAH	Diagenetic
Naphthalene	N0	2	X	X		
C1-Naphthalenes	N1	2	X			
C2-Naphthalenes	N2	2	X			
C3-Naphthalenes	N3	2	X			
C4-Naphthalenes	N4	2	X			
Biphenyl	B	2	X			
Dibenzofuran	DF	3	X			
Acenaphthylene	AY	3	X	X		
Acenaphthene	AE	3	X	X		
Fluorene	F0	3	X	X		
C1-Fluorenes	F1	3	X			
C2-Fluorenes	F2	3	X			
C3-Fluorenes	F3	3	X			
Anthracene	A0	3	X	X		
Phenanthrene	P0	3	X	X		
C1-Phenanthrenes/Anthracenes	PA1	3	X			
C2-Phenanthrenes/Anthracenes	PA2	3	X			
C3-Phenanthrenes/Anthracenes	PA3	3	X			
C4-Phenanthrenes/Anthracenes	PA4	3	X			
Retene	RET	3				X
Dibenzothiophene	DBT0	3	X		X	
C1-Dibenzothiophenes	DBT1	3	X		X	
C2-Dibenzothiophenes	DBT2	3	X		X	
C3-Dibenzothiophenes	DBT3	3	X		X	
C4-Dibenzothiophenes	DBT4	3	X		X	
Benzo(b)fluorene	BF	4	X			
Fluoranthene	FL0	4	X	X		
Pyrene	PY0	4	X	X		
C1-Fluoranthenes/Pyrenes	FP1	4	X			
C2-Fluoranthenes/Pyrenes	FP2	4	X			
C3-Fluoranthenes/Pyrenes	FP3	4	X			
C4-Fluoranthenes/Pyrenes	FP4	4	X			
Naphthobenzothiophenes	NBT0	4	X		X	
C1-Naphthobenzothiophenes	NBT1	4	X		X	
C2-Naphthobenzothiophenes	NBT2	4	X		X	
C3-Naphthobenzothiophenes	NBT3	4	X		X	
C4-Naphthobenzothiophenes	NBT4	4	X		X	
Benz[a]anthracene	BA0	4	X	X		
Chrysene/Triphenylene	C0	4	X	X		
C1-Chrysenes	BC1	4	X			
C2-Chrysenes	BC2	4	X			
C3-Chrysenes	BC3	4	X			
C4-Chrysenes	BC4	4	X			
Benzo[b]fluoranthene	BBF	5	X	X		
Benzo[k]fluoranthene	BKF	5	X	X		
Benzo[a]fluoranthene	BAF	5	X			
Benzo[e]pyrene	BEP	5	X			
Benzo[a]pyrene	BAP	5	X	X		
Perylene	PER	5	X			X
Indeno[1,2,3-cd]pyrene	IND	6	X	X		
Dibenz[a,h]anthracene	DA	5	X	X		
Benzo[g,h,i]perylene	GHI	6	X	X		
Carbazole	CAR	3				
Total	53		51	16	10	2

Table 3. Sediment Deposition Dates.

Radiogenic Core	Proximity	Chemistry Sample Depth Interval (ft)		BAP Conc (mg/kg)		Depositional Dates	Comments
		Top	Bottom	STL	NF		
GC-SED-01 Transect A	Top of Canal	1	2.5	1.5		1989-1998	S = 5.90 A = 4.92
		16	17	39		1925	
		19 n	**20 n**	87J	70	1894	
GC-SED-12 Transect D	Fulton	0	2	13		1982-2006	S = 1.08 A = 2.46
		13	14	43	22	1826	
GC-SED-21 Transect G	Between Citizens & Fulton	1.5	3	35		1986-1997	S = 3.08 A = 4.60
		7	8	12	16	1945	
GC-SED-87	4th Street Basin	4.4	6.2	40J	44	1934-1952	S = 1.30 A = 3.01
		12.7 n	**13.3 n**	21		1909	
		19 n	**20 n**	<0.078		1829	
GC-SED-88	6th Street Basin	0.5	1	34		2002-2004	S = 2.84 A = 6.21
		9.9 n	**10.4 n**	47J		1948-1946	
		15.9 n	**16.9 n**	25J	62	1841	
GC-SED-31 Transect K	Citizens	2.5	4.5	20	18	1980-1990	S = 3.22 A = 5.27
		11.5 n	**12.5 n**	380J		1923	
		16.5 n	**18 n**	38J		1846	

n	**Native sediment**	BAP	Benzo(a)pyrene
S	Sedimentation rate in $g/cm^2/yr$	STL	Traditional EPA 8270 Method
A	Sediment accumulation rate in cm/yr	NF	Forensic PAH Method
NA	Not available	J	Estimated concentraiton
		<	Below detection limit

Table 4. Summary of Hydrocarbon Chemistry.

Sample ID [1]	EPAPAH mg/kg	TPH mg/kg	EPAPAH / TPH	Percentage [2] Petroleum Product	Percentage [2] Tar and Combustion	PAH Source Ratios FL0 / PY0	PAH Source Ratios (BBF+BKF) / BAP	Precision [3] EPAPAH	Precision [3] TPH	Precision [3] EPAPAH / TPH	Precision [3] FL0 / PY0	Precision [3] (BBF+BKF) / BAP
GC-SED-01 (19-20)	3,610	17,000	0.21	22%	78%	0.67	0.94					
GC-SED-02 (17.1-18.1)	1,480	10,000	0.15	46%	54%	0.67	0.96					
GC-SED-03 (0-1.5)	207	5,500	0.04	86%	14%	1.21	1.67					
GC-SED-04 (10.3-11.3)	2,880	27,000	0.11	61%	39%	0.71	1.16	9%	16%	25%	2%	3%
GC-SED-04 (10.3-11.3)X	3,140	23,000	0.14	50%	50%	0.70	1.19					
GC-SED-05 (0-2)	269	5,700	0.05	83%	17%	0.64	1.15	6%	30%	25%	2%	2%
GC-SED-05 (0-2)D	254	4,200	0.06	78%	22%	0.66	1.13					
GC-SED-05 (0-2)X	196	2,300	0.09	69%	31%	0.70	1.05	43%	36%	8%	5%	1%
GC-SED-05 (0-2)DX	126	1,600	0.08	71%	29%	0.67	1.04					
GC-SED-07 (7.5-8.5)	260	14,000	0.02	93%	7%	0.68	1.19	21%	13%	8%	1%	7%
GC-SED-07 (7.5-8.5)D	321	16,000	0.02	93%	7%	0.67	1.27					
GC-SED-08 (10.5-11.5)	34,300	110,000	0.31	< 1%	100%	0.71	1.02	8%	20%	12%	3%	2%
GC-SED-08 (10.5-11.5)X	31,700	90,000	0.35	< 1%	100%	0.70	1.04					
GC-SED-09 (6-7)	12,000	87,000	0.14	50%	50%	0.64	0.97	8%	22%	13%	1%	0%
GC-SED-09 (6-7)X	11,000	70,000	0.16	42%	58%	0.65	0.96					
GC-SED-10 (0-1.5)	435	10,000	0.04	84%	16%	0.68	1.10	8%	0%	8%	0%	7%
GC-SED-10 (0-1.5)D	402	10,000	0.04	85%	15%	0.68	1.18					
GC-SED-11 (1-3)	737	15,000	0.05	82%	18%	0.68	1.07					
GC-SED-12 (13-14)	558	7,200	0.08	72%	28%	0.65	1.18					
GC-SED-13B (14.6-15.6)	14,100	66,000	0.21	22%	78%	0.69	1.00					
GC-SED-14 (5.5-6.5)	15,400	80,000	0.19	29%	71%	0.71	1.03					
GC-SED-15 (0-0.75)	106	5,400	0.02	93%	7%	0.73	1.20	9%	12%	21%	2%	2%
GC-SED-15 (0-0.75)D	97.1	6,100	0.02	94%	6%	0.71	1.23					
GC-SED-16 (0-2)	178	7,000	0.03	91%	9%	0.83	1.24					
GC-SED-17 (0-2)	202	7,600	0.03	90%	10%	0.70	1.20					
GC-SED-18 (7-8)	2,330	12,000	0.19	29%	71%	0.70	1.02					
GC-SED-19C (1.5-2)	333	15,000	0.02	92%	8%	0.77	1.21					
GC-SED-20 (4-5)	354	19,000	0.02	93%	7%	0.74	1.19					
GC-SED-21B (7-8)	218	12,000	0.02	93%	7%	0.76	1.11					
GC-SED-22B (19.3-20)	42.6	640	0.07	76%	24%	0.78	1.07					
GC-SED-23 (17.5-19)	239	1,800	0.13	51%	49%	0.66	1.23					
GC-SED-24 (12.6-13.4)	790	5,400	0.15	46%	54%	0.66	1.25					
GC-SED-25 (9-10)	29,000	160,000	0.18	34%	66%	0.67	1.02					
GC-SED-26 (5.3-5.8)	1,690	8,700	0.19	29%	71%	0.71	1.06					
GC-SED-27 (4.9-5.4)	5,900	55,000	0.11	61%	39%	0.69	1.17					
GC-SED-28 (4.9-5.8)	33.5	1,800	0.02	93%	7%	0.73	1.17					
GC-SED-29 (7.4-8.4)	2,480	11,000	0.23	17%	83%	0.69	1.07					
GC-SED-30 (3.5-5.5)	220	14,000	0.02	94%	6%	0.78	1.25					
GC-SED-31 (2.5-4.5)	302	22,000	0.01	95%	5%	0.71	1.22					
GC-SED-32 (5.9-6.9)	840	31,000	0.03	90%	10%	0.70	1.18					
GC-SED-33 (1.5-3)	211	16,000	0.01	95%	5%	0.74	1.17	32%	36%	4%	1%	2%
GC-SED-33 (1.5-3)D	290	23,000	0.01	95%	5%	0.75	1.15					
GC-SED-34B (2-3)	641	33,000	0.02	93%	7%	0.66	1.11	4%	0%	4%	3%	1%
GC-SED-34B (2-3)D	670	33,000	0.02	93%	7%	0.68	1.10					
GC-SED-35 (15.3-17.3)	5,760	37,000	0.16	43%	57%	0.66	1.02					
GC-SED-36 (2.5-4.5)	403	26,000	0.02	94%	6%	0.70	1.17					
GC-SED-37B (7-8)	7,690	71,000	0.11	60%	40%	0.74	1.25					
GC-SED-38 (5.1-6.1)	1,870	41,000	0.05	83%	17%	0.65	1.07					

Table 4. Summary of Hydrocarbon Chemistry (continued).

Sample ID [1]	EPAPAH mg/kg	TPH mg/kg	EPAPAH / TPH	Percentage [2] Petroleum Product	Percentage [2] Tar and Combustion	PAH Source Ratios FL0 / PY0	PAH Source Ratios (BBF+BKF) / BAP	Precision [3] EPAPAH	Precision [3] TPH	Precision [3] EPAPAH / TPH	Precision [3] FL0 / PY0	Precision [3] (BBF+BKF) / BAP
GC-SED-39 (4.5-5.5)	13,900	170,000	0.08	70%	30%	0.61	1.00					
GC-SED-40 (5-6)	3,720	64,000	0.06	79%	21%	0.68	1.10					
GC-SED-41 (7.3-8.3)	5,370	40,000	0.13	51%	49%	0.63	1.05					
GC-SED-43 (7.3-8.3)	19,500	170,000	0.11	58%	42%	0.59	1.03					
GC-SED-44 (5.6-6.1)	12,800	110,000	0.12	57%	43%	0.62	1.08					
GC-SED-45C (1-1.5)	15,800	100,000	0.16	42%	58%	0.64	1.04					
GC-SED-46C (5-5.5)	16,500	150,000	0.11	60%	40%	0.58	1.00					
GC-SED-47 (1.5-2.5)	16,000	140,000	0.11	58%	42%	0.60	1.03					
GC-SED-48 (5-5.8)	14,100	110,000	0.13	53%	47%	0.62	1.04					
GC-SED-49 (10-11)	3,020	13,000	0.23	15%	85%	0.71	1.09					
GC-SED-50 (2-5)	12,300	80,000	0.15	44%	56%	0.61	1.07					
GC-SED-51 (0-1.5)	2,500	44,000	0.06	79%	21%	0.66	1.10	24%	19%	6%	1%	2%
GC-SED-51 (0-1.5)D	3,180	53,000	0.06	78%	22%	0.65	1.12					
GC-SED-52 (3-6)	14,800	180,000	0.08	70%	30%	0.59	1.00					
GC-SED-53 (0.5-1.5)	6,400	65,000	0.10	64%	36%	0.64	0.90					
GC-SED-54B (4.5-5.7)	17,100	120,000	0.14	48%	52%	0.63	1.03					
GC-SED-55 (1.5-2.5)	288	11,000	0.03	91%	9%	0.68	1.18					
GC-SED-56 (5.8-6.2)	11,500	100,000	0.12	58%	42%	0.61	1.04					
GC-SED-57 (7-9)	1,250	27,000	0.05	83%	17%	0.71	1.13					
GC-SED-58C (8-10)	6,800	31,000	0.22	20%	80%	0.68	1.09					
GC-SED-59 (6-7.25)	3,420	19,000	0.18	34%	66%	0.64	1.03					
GC-SED-60B (6.8-8)	3,140	63,000	0.05	82%	18%	0.65	1.01	18%	21%	3%	4%	4%
GC-SED-60B (6.8-8)D	3,770	78,000	0.05	82%	18%	0.63	1.06					
GC-SED-62C (3-4)	16,600	100,000	0.17	39%	61%	0.62	1.06					
GC-SED-63 (3-3.5)	1,560	30,000	0.05	81%	19%	0.65	1.05					
GC-SED-64D (2-4)	13,300	120,000	0.11	60%	40%	0.62	1.04					
GC-SED-65 (0.5-1.25)	4,580	46,000	0.10	64%	36%	0.59	1.01					
GC-SED-66 (11.5-12.5)	26,900	120,000	0.22	18%	82%	0.70	1.06					
GC-SED-67 (8-8.4)	3,420	51,000	0.07	75%	25%	0.58	0.98					
GC-SED-68 (2.2-3.1)	6,130	82,000	0.07	73%	27%	0.63	0.98					
GC-SED-69 (6-7)	437	5,900	0.07	73%	27%	0.71	1.35					
GC-SED-70B (4-5)	2,620	22,000	0.12	56%	44%	0.75	1.12					
GC-SED-71C (1.5-2.5)	2,690	38,000	0.07	74%	26%	0.65	1.05					
GC-SED-72 (13.5-14.5)	11,100	68,000	0.16	40%	60%	0.73	1.04					
GC-SED-73E (3.8-8.4)	309	7,400	0.04	85%	15%	0.98	1.40	6%	29%	24%	17%	10%
GC-SED-73E (3.8-8.4)D	293	5,500	0.05	81%	19%	1.16	1.55					
GC-SED-74 (5.3-6.3)	1,540	39,000	0.04	86%	14%	0.71	1.14					
GC-SED-75C (0-0.7)	57.4	3,300	0.02	94%	6%	1.08	1.56	1%	3%	4%	8%	1%
GC-SED-75C (0-0.7)D	56.8	3,400	0.02	94%	6%	1.00	1.55					
GC-SED-76C (2.5-3.4)	165	11,000	0.01	95%	5%	0.88	1.31					
GC-SED-77 (14.5-15.4)	1,260	15,000	0.08	69%	31%	0.73	1.10					
GC-SED-78B (2.5-5)	274	16,000	0.02	94%	6%	1.38	1.74					
GC-SED-79 (2.5-3.5)	776	30,000	0.03	91%	9%	0.73	1.05					
GC-SED-80 (0-2)	143	18,000	0.01	97%	3%	0.71	1.26					
GC-SED-81 (8-11)	1,320	27,000	0.05	82%	18%	0.63	1.00					
GC-SED-82 (12-12.8)	1,900	28,000	0.07	75%	25%	0.61	1.02					
GC-SED-83 (0-2)	36.5	5,200	0.01	98%	2%	0.48	1.34					
GC-SED-84 (6-7)	3,330	16,000	0.21	24%	76%	0.68	1.12					
GC-SED-85B (8.5-9.3)	1,800	52,000	0.03	87%	13%	0.75	1.17					
GC-SED-86 (0-1)	785	57,000	0.01	95%	5%	0.68	1.12					

Table 4. Summary of Hydrocarbon Chemistry (continued).

Sample ID [1]	EPAPAH mg/kg	TPH mg/kg	EPAPAH / TPH	Percentage [2] Petroleum Product	Percentage [2] Tar and Combustion	PAH Source Ratios FL0 / PY0	PAH Source Ratios (BBF+BKF) / BAP	Precision [3] EPAPAH	Precision [3] TPH	Precision [3] EPAPAH / TPH	Precision [3] FL0 / PY0	Precision [3] (BBF+BKF) / BAP
GC-SED-87 (4.4-6.2)	715	64,000	0.01	96%	4%	0.65	1.18	3%	0%	3%	7%	2%
GC-SED-87 (4.4-6.2)D	694	64,000	0.01	96%	4%	0.70	1.21					
GC-SED-88 (15.9-16.9)	3,230	17,000	0.19	30%	70%	0.64	1.15					
GC-SED-89 (12.8-13.8)	7,010	47,000	0.15	45%	55%	0.65	1.17					
GC-SED-90B (6.5-7)	4,570	32,000	0.14	48%	52%	0.68	1.10					
GC-SED-91 (10.2-11.2)	24,600	230,000	0.11	61%	39%	0.58	1.02					
GC-SED-92 (0-2)	351	32,000	0.01	96%	4%	0.69	1.22					
GC-SED-93 (0-1)	670	66,000	0.01	96%	4%	0.64	1.15					
GC-SED-94 (19-20)	5,060	20,000	0.25	7%	93%	0.66	1.06					
GC-SED-95 (3.5-4.5)	580	34,000	0.02	94%	6%	0.80	1.20					
GC-SED-96 (14-15)	3,420	18,000	0.19	30%	70%	0.65	0.96					
GC-SED-97 (8.5-9.5)	5,470	95,000	0.06	79%	21%	0.62	1.07					
GC-SED-98 (1-2)	119	8,500	0.01	95%	5%	0.80	1.37					
GC-SED-99 (3.5-4.5)	5,220	100,000	0.05	81%	19%	0.61	1.10					
GC-SED-100 (5-6)	9,900	150,000	0.07	76%	24%	0.62	1.00					
GC-SED-101 (7.9-9.1)	1,720	13,000	0.13	52%	48%	0.63	1.03					
GC-SED-102 (2-4)	15,800	190,000	0.08	70%	30%	0.62	1.03	19%	19%	0%	4%	1%
GC-SED-102 (2-4)D	19,200	230,000	0.08	70%	30%	0.60	1.02					
GC-SED-103 (8.1-9.1)	6,040	64,000	0.09	65%	35%	0.63	1.03					
GC-SED-104 (3.7-5.1)	120	4,500	0.03	90%	10%	0.81	1.18	47%	61%	15%	7%	1%
GC-SED-104 (3.7-5.1)D	74.9	2,400	0.03	89%	11%	0.75	1.19					
GC-SED-105 (2.5-4)	13,200	130,000	0.10	63%	37%	0.64	1.06					
GC-SED-RH 039	170,000	830,000	0.20	25%	75%	0.68	0.97					
CGMW-07I	157,000	570,000	0.28	< 1%	100%	0.69	1.04	5%	4%	1%	0%	4%
CGMW-07ID	150,000	550,000	0.27	< 1%	100%	0.69	1.00					
CGMW-08I	145,000	620,000	0.23	14%	86%	0.70	1.04					
GC-GP-05 (33-35)	26,600	120,000	0.22	19%	81%	0.70	1.07					
GC-GP-06 (17-17.1)	77.7	8,100	0.01	97%	3%	0.51	0.85					
GC-GP-07 (2-3)	43.0	10,000	0.00	99%	1%	0.98	1.64					
GC-GP-13 (6-8)	0.96	150	0.01	98%	2%	0.88	1.81	33%	18%	15%	1%	12%
GC-GP-13 (6-8)D	1.33	180	0.01	97%	3%	0.89	1.61					
GC-GP-15 (9-9.5)	0.62	1,200	0.00	100%	< 1%	0.65	1.14					
CGSB-54B (0-0.25)	2.92	12,000	0.00	100%	< 1%	0.44	1.51					
CGSB-57 (0-0.1)	3.31	14,000	0.00	100%	< 1%	0.42	2.09					
GC-GP-06 (0-0.1)	7.62	27,000	0.00	100%	< 1%	0.66	1.70					
GC-GP-07 (0-0.1)	4.01	13,000	0.00	100%	< 1%	0.30	2.16					
GC-GP-13 (0-0.1)	3.44	28,000	0.00	100%	< 1%	0.57	1.79					
GC-GP-15 (0-0.1)	13.1	27,000	0.00	100%	< 1%	0.18	2.30					
FS-Halleck St Row	145,000	480,000	0.30	< 1%	100%	1.15	1.58	7%	0%	7%	1%	0%
FS-Halleck St Row	135,000	480,000	0.28	< 1%	100%	1.17	1.57					
FS-RED HOOK-1	162,000	560,000	0.29	< 1%	100%	1.14	1.44	2%	4%	1%	4%	0%
FS-RED HOOK-1	166,000	580,000	0.29	< 1%	100%	1.19	1.44					
FS-RED HOOK-2	178,000	590,000	0.30	< 1%	100%	1.13	1.45					
FS-RED HOOK-3	184,000	630,000	0.29	< 1%	100%	1.17	1.45					
FS-RED HOOK-4	167,000	600,000	0.28	< 1%	100%	1.17	1.48					
FS-HALLECK ST ROW-2	74,400	430,000	0.17	37%	63%	1.24	1.63					
FS-HALLECK ST ROW-3	164,000	590,000	0.28	< 1%	100%	1.09	1.41					
FS-COURT ST ROW-1	175,000	610,000	0.29	< 1%	100%	1.17	1.43					

Table 4. Summary of Hydrocarbon Chemistry (continued).

Sample ID [1]	EPAPAH mg/kg	TPH mg/kg	EPAPAH / TPH	Percentage [2] Petroleum Product	Percentage [2] Tar and Combustion	PAH Source Ratios FL0 / PY0	PAH Source Ratios (BBF+BKF) / BAP	Precision [3] EPAPAH	Precision [3] TPH	Precision [3] EPAPAH / TPH	Precision [3] FL0 / PY0	Precision [3] (BBF+BKF) / BAP
Lab Ref Crude Oil R1	1,340	590,000	0.00	100%	< 1%	0.29	3.82	7%	4%	5%	13%	26%
Lab Ref Crude Oil R2	1,210	560,000	0.00	100%	< 1%	0.31	5.27					
Lab Ref Crude Oil R3	1,160	570,000	0.00	100%	< 1%	0.23	2.28					
Lab Ref Crude Oil R4	1,110	530,000	0.00	100%	< 1%	0.35	4.91					
Lab Ref Crude Oil R5	1,160	590,000	0.00	100%	< 1%	0.31	3.73					
Lab Ref Crude Oil R6	1,130	560,000	0.00	100%	< 1%	0.30	3.87					

Notes:

1 Sample IDs ending with "D" are laboratory duplicates and "X" are re-extracted samples.

2 Percent tar was calculated as (RS - RP) / (RT - RP) * 100, where R is the ratio of EPAPAH/TPH, S is the sample, P is the average value for the pavement samples (0.0002796) and T is the average value for tars from the former Citizens MGP monitoring wells (0.2610).
The percent petroleum product was calculated as 100 - percent tar

3 Precision for duplicate samples is calculated using the formula ABS (S - D) / Average (S and D), where S is the sample and D is the duplicate.
The precision for more than two replicates is calculated as the standard deviation / average (see Lab Ref Crude Oil replicates).

Attachment B
Figures

Figure 1. Gowanus Canal Forensic Sampling Locations.

Figure 2a. High Resolution Hydrocarbon Fingerprints for Samples Near Transect A.

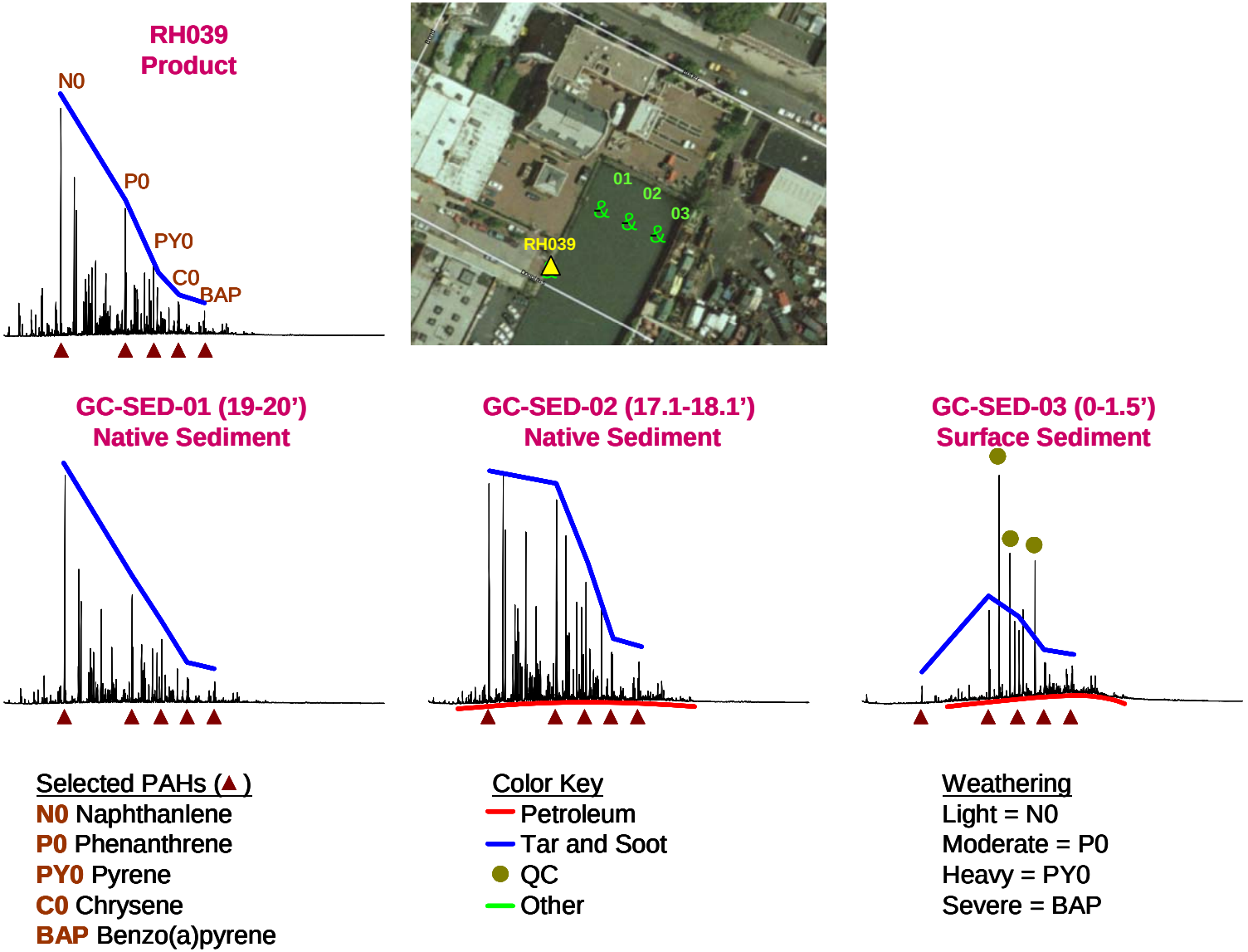


Figure 2b. High Resolution Hydrocarbon Fingerprints for Samples Near Transect C.

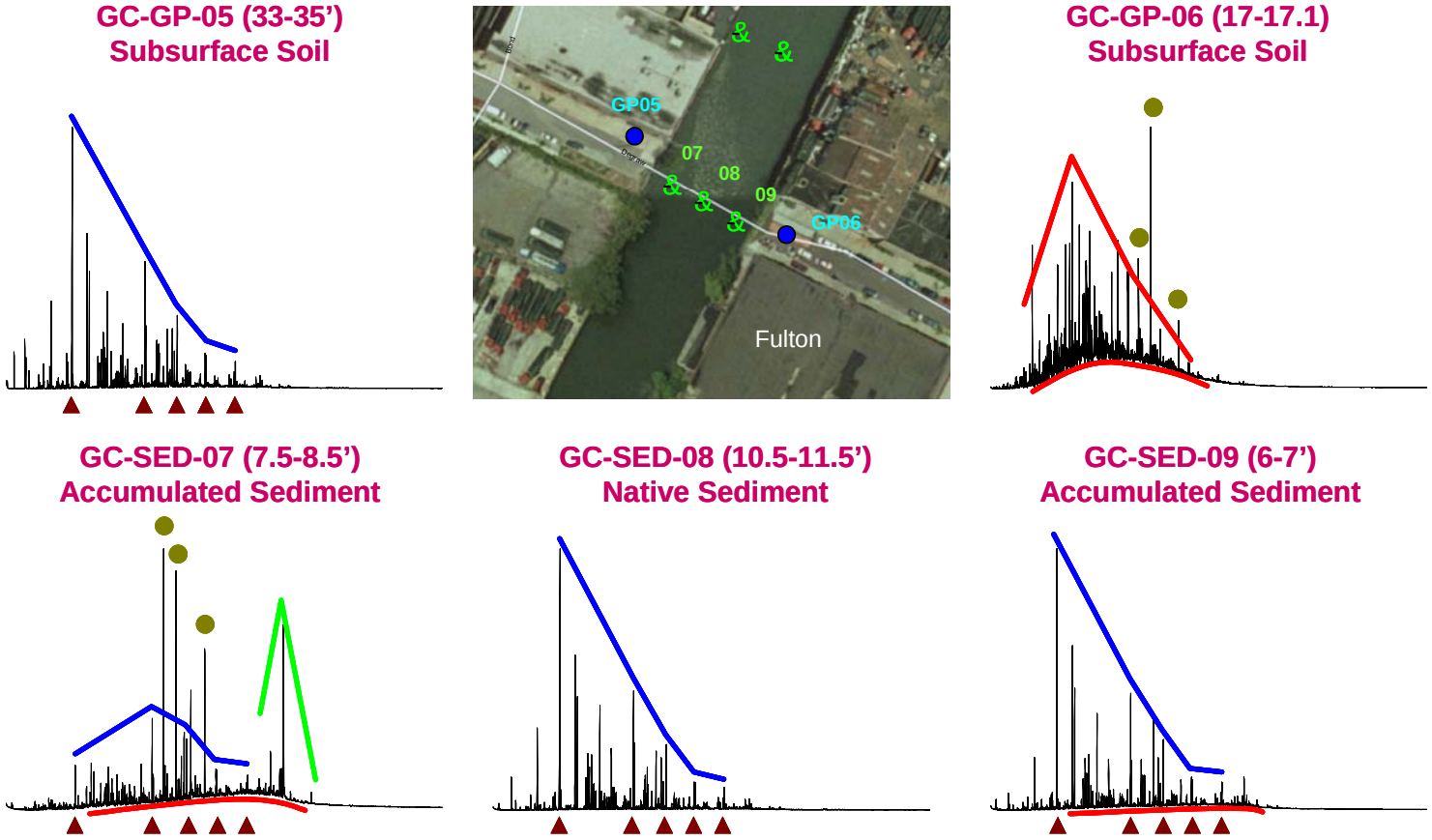
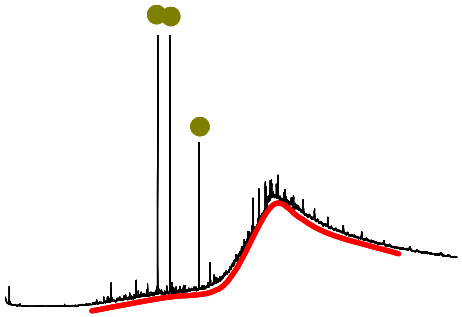
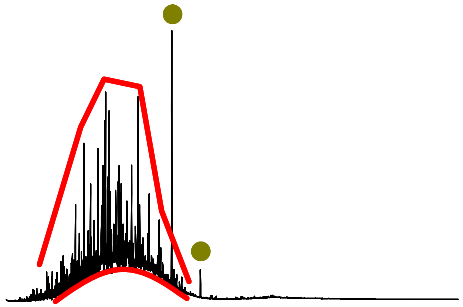


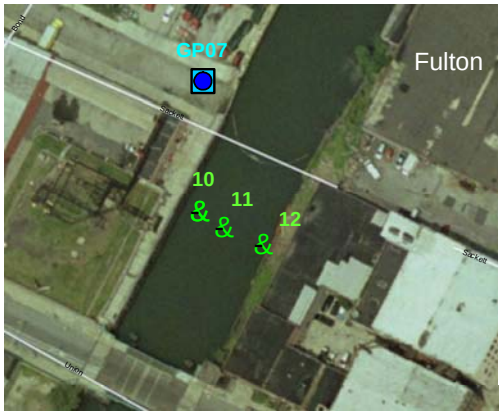
Figure 2c. High Resolution Hydrocarbon Fingerprints for Samples Near Transect D.

GC-GP-07 (0-0.1')
Pavement

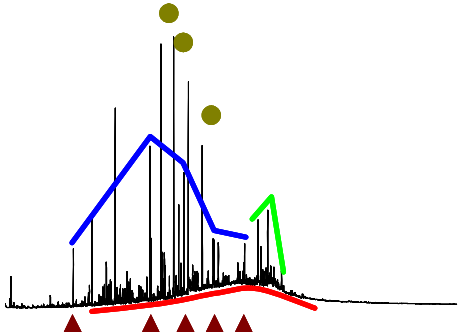


GC-GP-07 (2-3')
Subsurface Soil

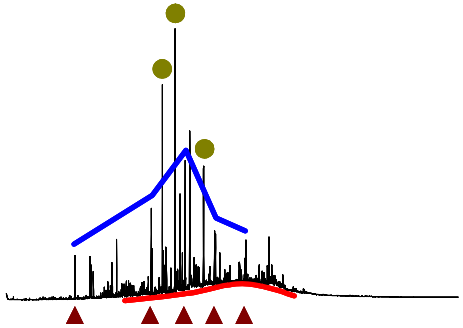




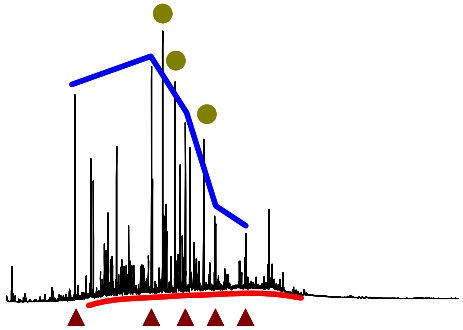
GC-SED-10 (0-1.5')
Surface Sediment



GC-SED-11 (1-3')
Surface Sediment



GC-SED-12 (13-14')
Accumulated Sediment



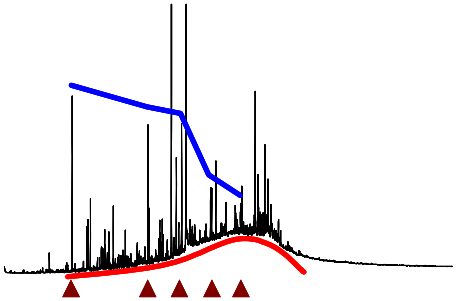
Selected PAHs (▲)
N0 Naphthanlene
P0 Phenanthrene
PY0 Pyrene
C0 Chrysene
BAP Benzo(a)pyrene

Color Key
Petroleum
Tar and Soot
QC
Other

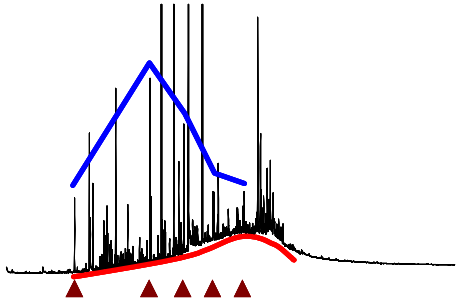
Weathering
Light = N0
Moderate = P0
Heavy = PY0
Severe = BAP

Figure 2d. High Resolution Hydrocarbon Fingerprints for Samples From Transect F.

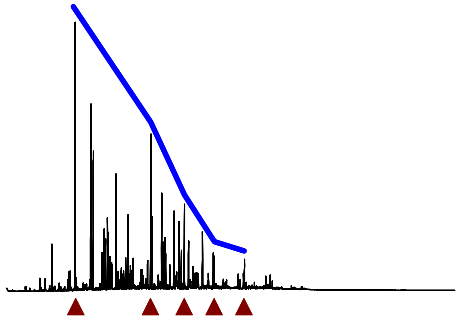
GC-SED-16 (0-2')
Surface Sediment



GC-SED-17 (0-2')
Surface Sediment



GC-SED-18 (7-8')
Native Sediment



Selected PAHs (▲)
N0 Naphthanlene
P0 Phenanthrene
PY0 Pyrene
C0 Chrysene
BAP Benzo(a)pyrene

Color Key
Petroleum
Tar and Soot
QC
Other

Weathering
Light = N0
Moderate = P0
Heavy = PY0
Severe = BAP

Figure 2e. High Resolution Hydrocarbon Fingerprints for Samples Near Transect G.

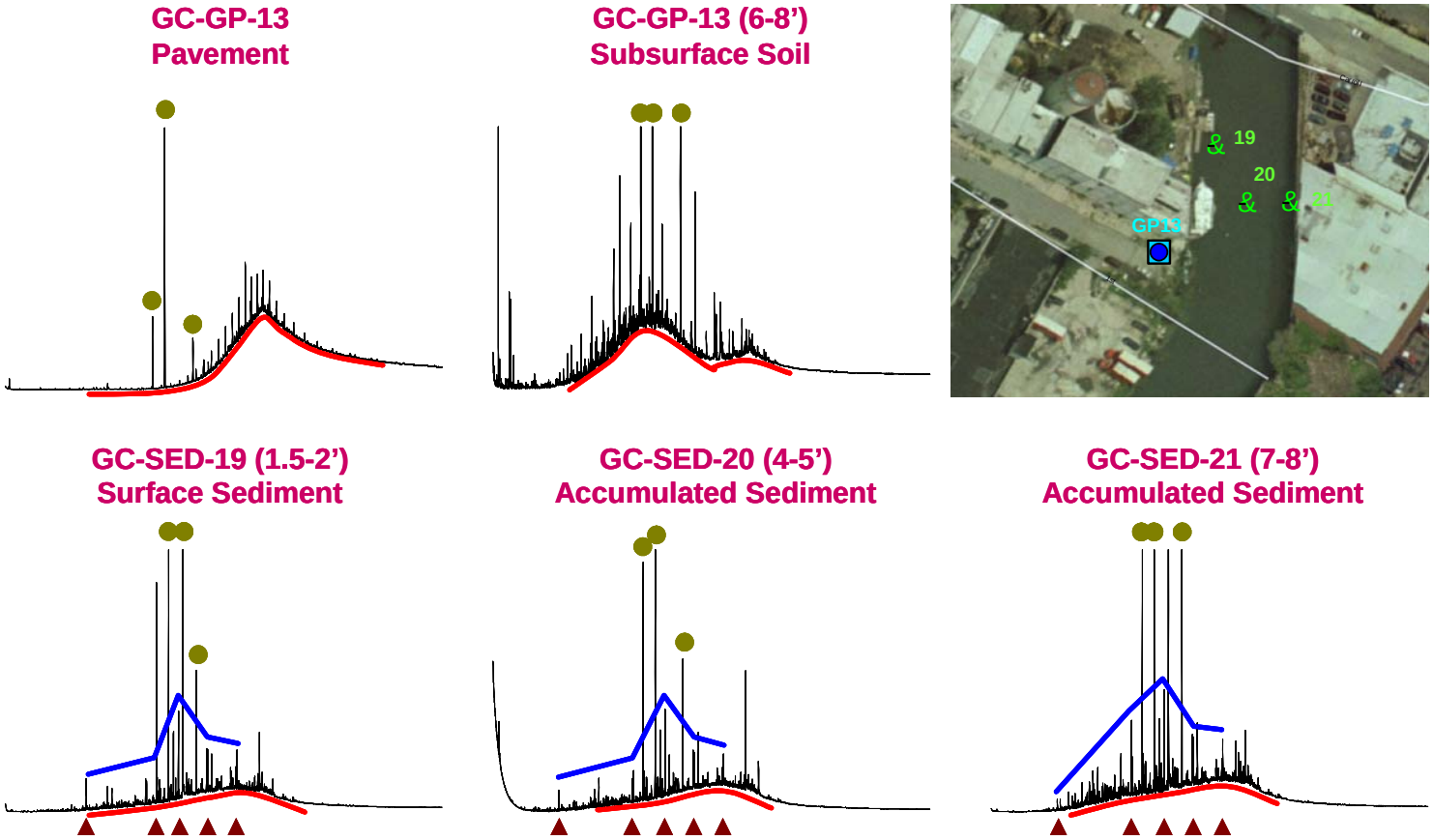


Figure 2f. High Resolution Hydrocarbon Fingerprints for Samples Near Transect H.

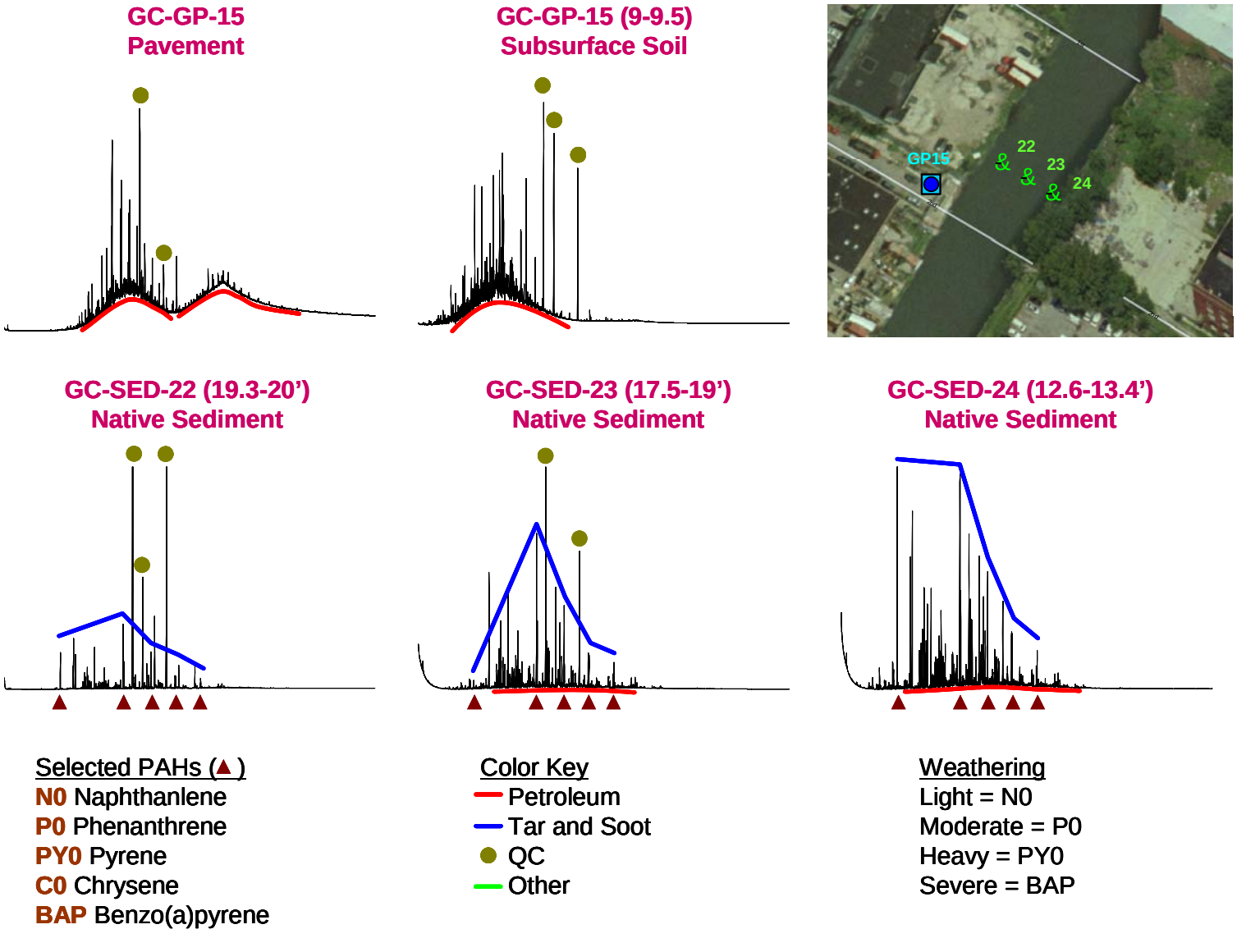


Figure 2g. High Resolution Hydrocarbon Fingerprints for Samples Near Transect O.

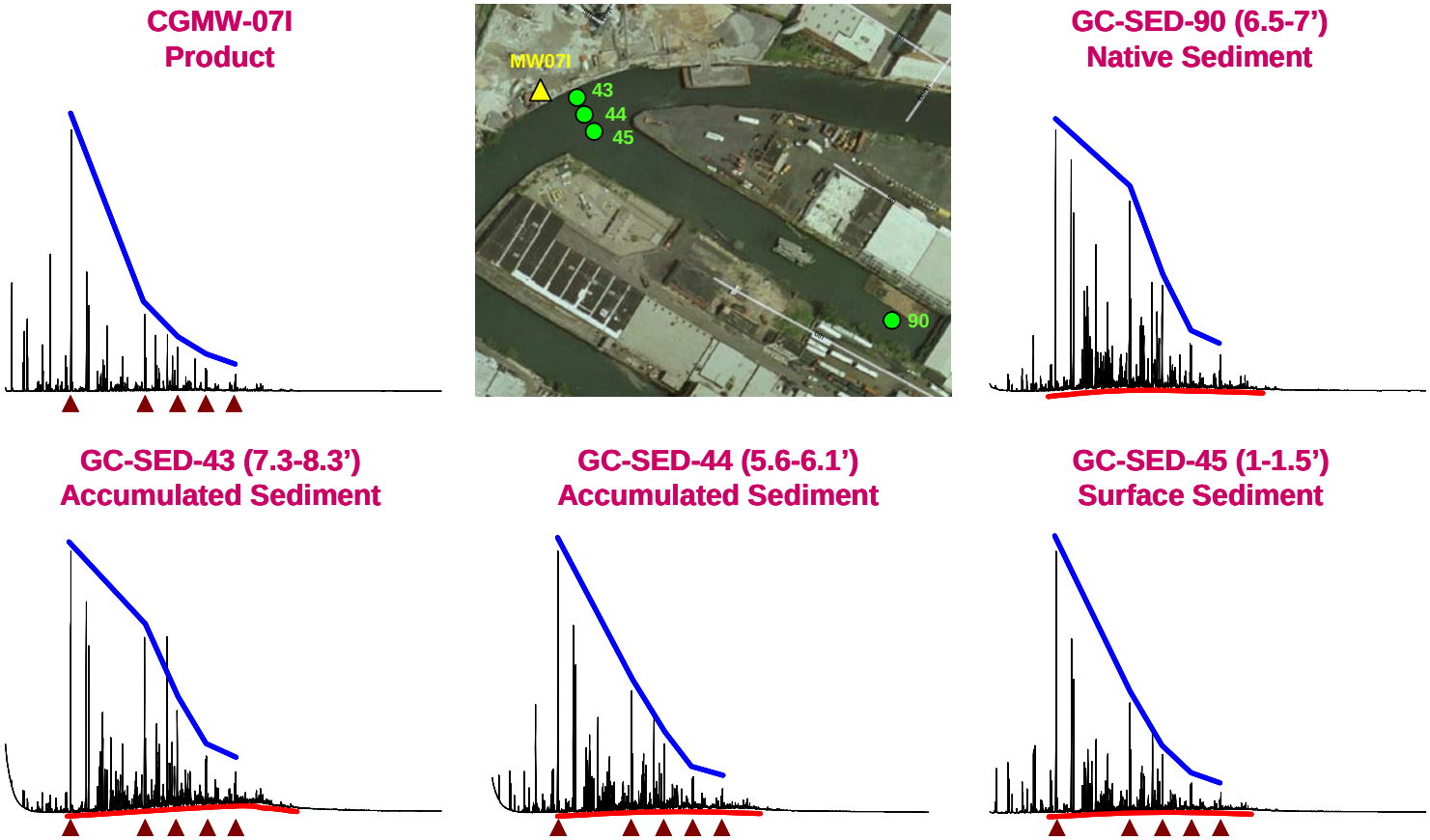


Figure 2h. High Resolution Hydrocarbon Fingerprints for Samples Near Transect R.

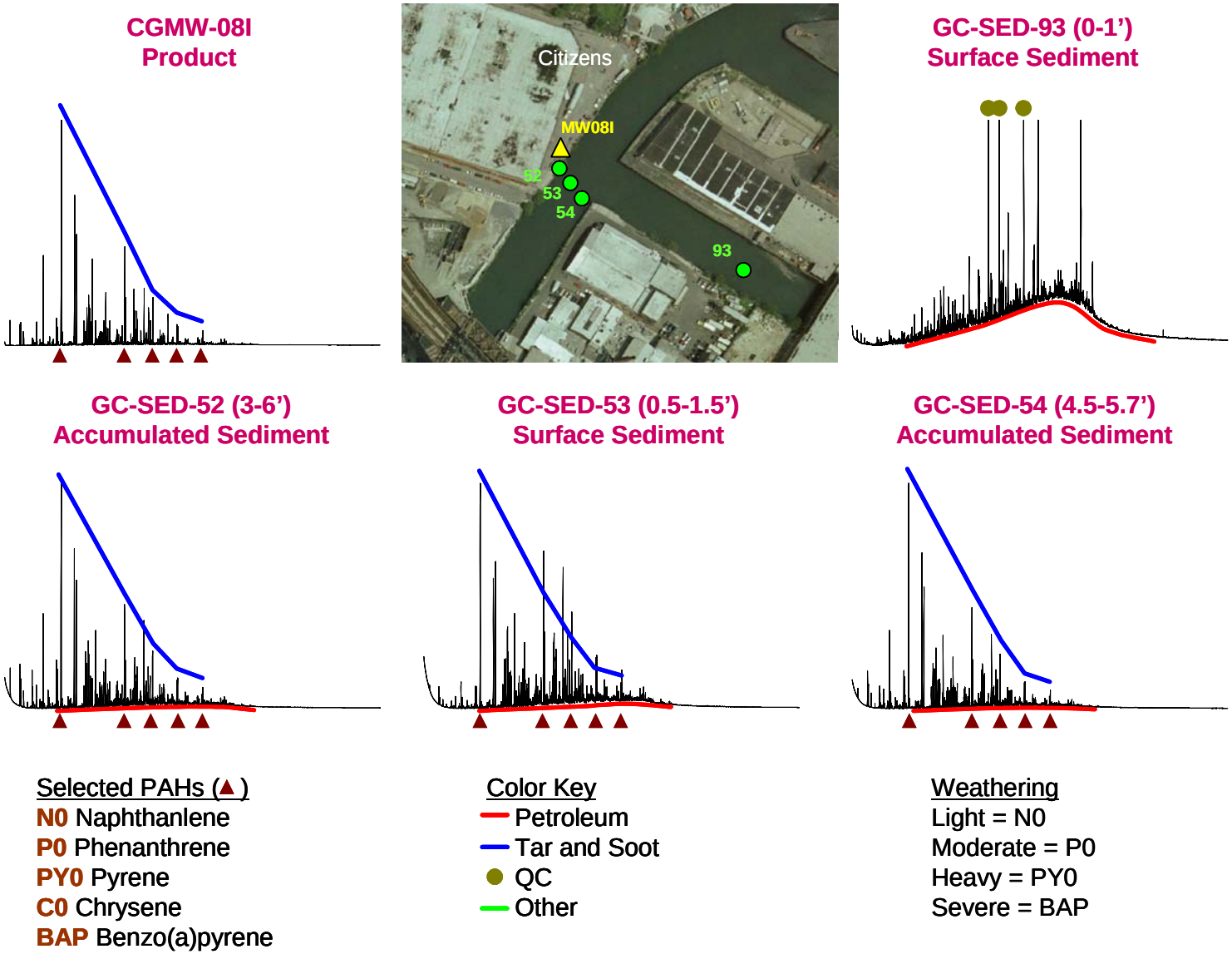
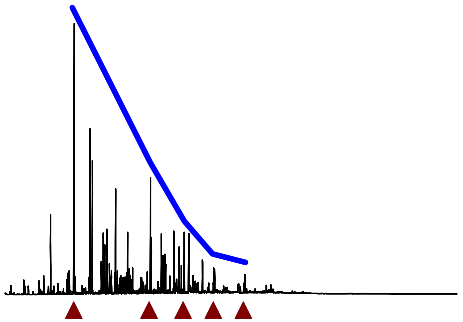


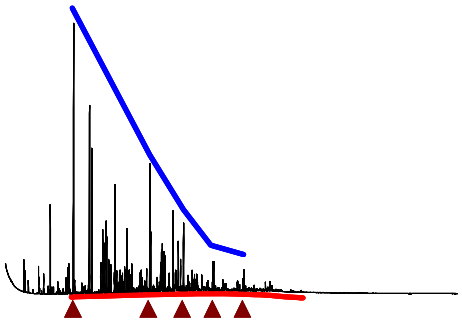
Figure 2i. High Resolution Hydrocarbon Fingerprints for Samples Near Transect U.

GC-SED-94 (19-20')
Native Sediment

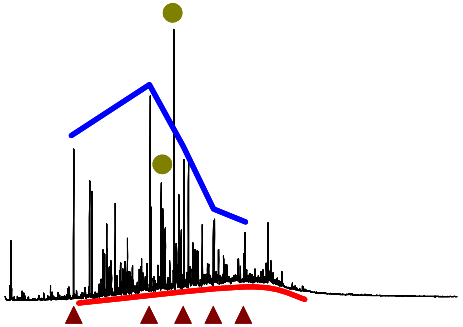


GC-SED-61
No Forensic Sample

GC-SED-62 (3-4')
Accumulated Sediment



GC-SED-63 (3-3.5')
Accumulated Sediment



Selected PAHs (▲)
N0 Naphthanlene
P0 Phenanthrene
PY0 Pyrene
C0 Chrysene
BAP Benzo(a)pyrene

Color Key
Petroleum
Tar and Soot
QC
Other

Weathering
Light = N0
Moderate = P0
Heavy = PY0
Severe = BAP

Figure 2j. High Resolution Hydrocarbon Fingerprints for Samples from Transects V & BB.

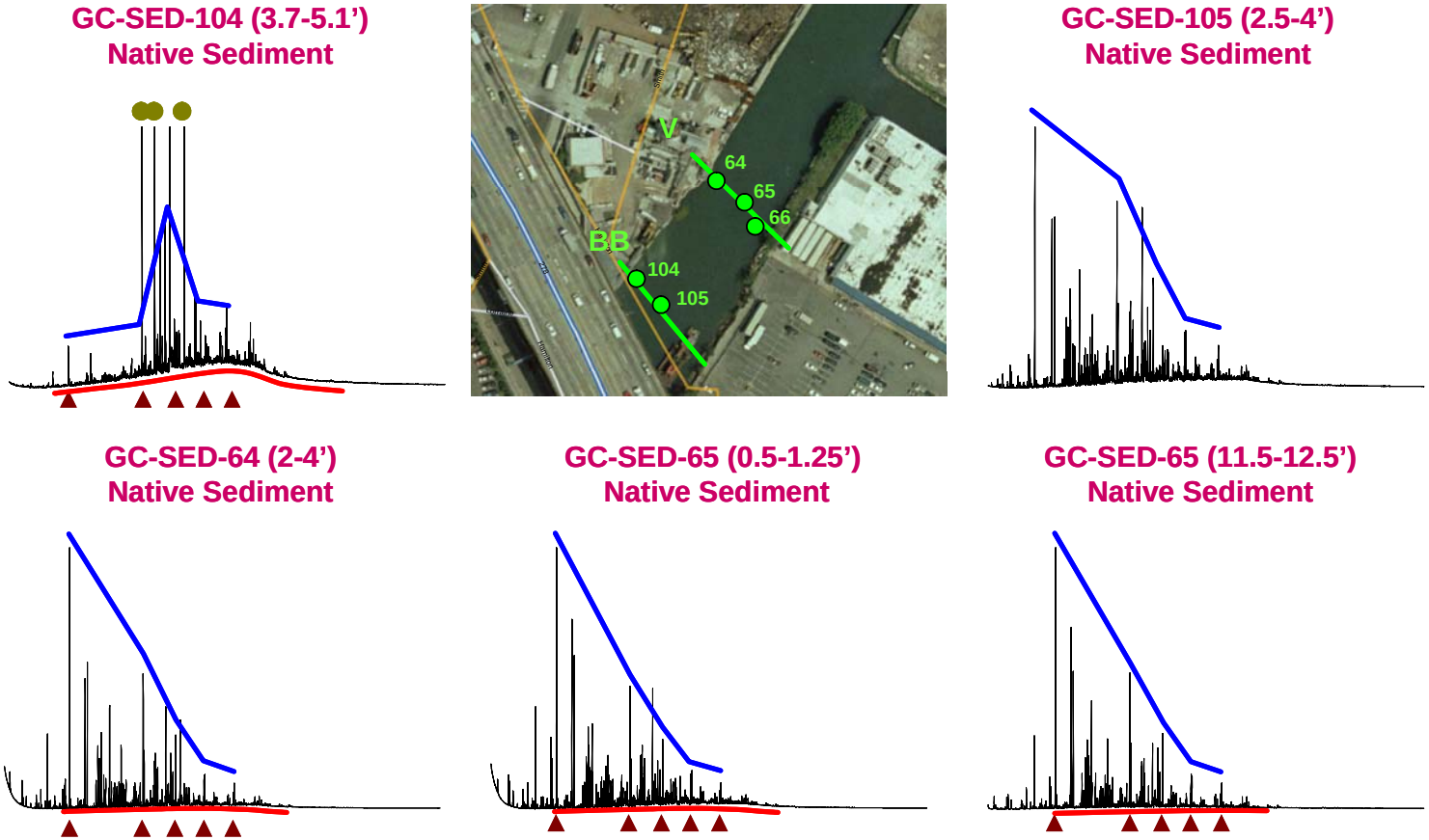
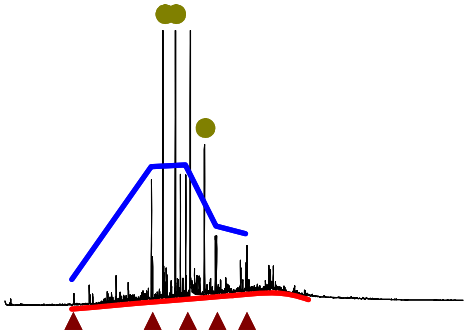
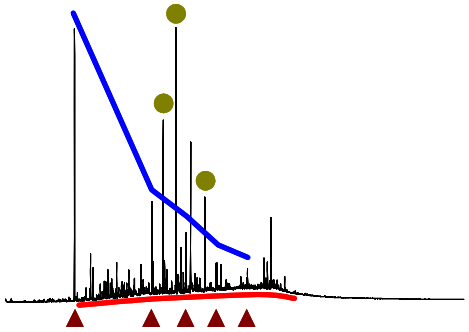


Figure 2k. High Resolution Hydrocarbon Fingerprints for Samples From Transect Y.

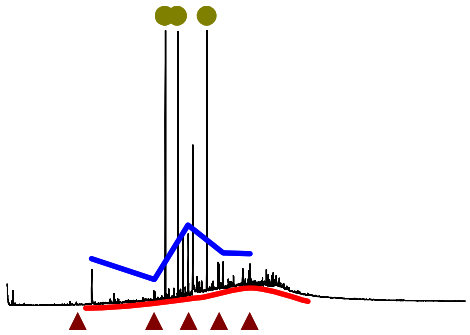
GC-SED-73 (3.8-4.8)
Accumulated Sediment



GC-SED-74 (5.3-6.3)
Accumulated Sediment



GC-SED-75 (0-0.7)
Surface Sediment



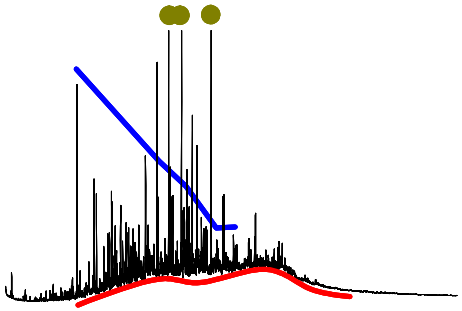
Selected PAHs (▲)
N0 Naphthanlene
P0 Phenanthrene
PY0 Pyrene
C0 Chrysene
BAP Benzo(a)pyrene

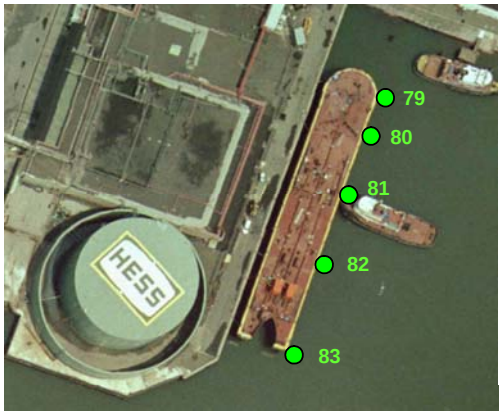
Color Key
Petroleum
Tar and Soot
QC
Other

Weathering
Light = N0
Moderate = P0
Heavy = PY0
Severe = BAP

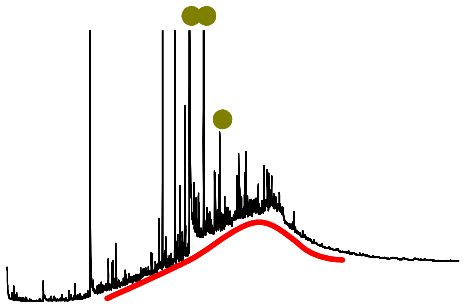
Figure 2l. High Resolution Hydrocarbon Fingerprints for Samples From Transect AA.

GC-SED-79 (2.5-3.5)
Accumulated Sediment

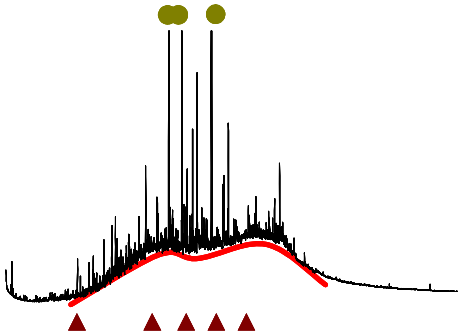




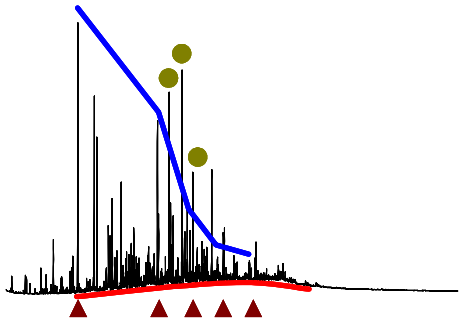
GC-SED-83 (0-2')
Surface Sediment



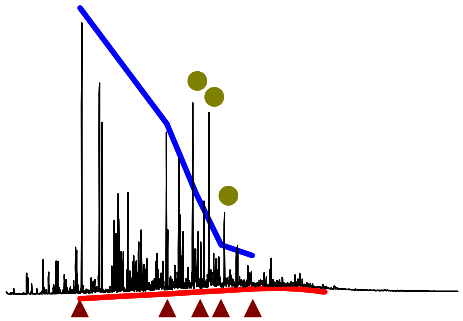
GC-SED-80 (0-2')
Surface Sediment



GC-SED-81 (8-11')
Accumulated Sediment



GC-SED-82 (12-12.8')
Accumulated Sediment



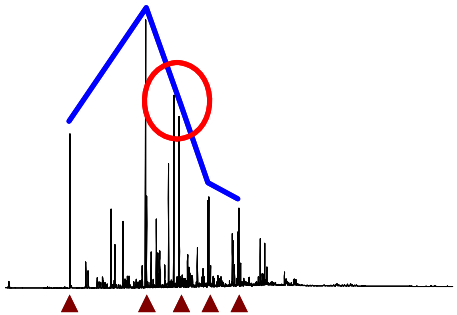
Selected PAHs (▲)
N0 Naphthanlene
P0 Phenanthrene
PY0 Pyrene
C0 Chrysene
BAP Benzo(a)pyrene

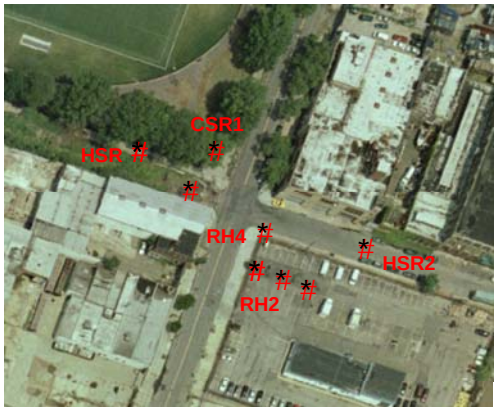
Color Key
Petroleum
Tar and Soot
QC
Other

Weathering
Light = N0
Moderate = P0
Heavy = PY0
Severe = BAP

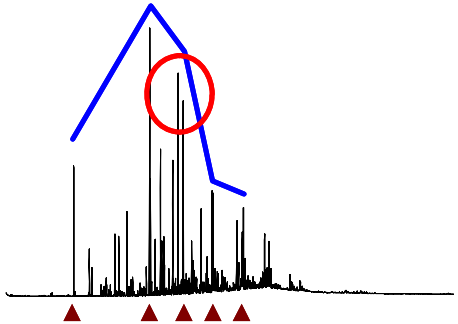
Figure 2m. High Resolution Hydrocarbon Fingerprints for Samples From Red Hook.

FS-Halleck St Row Surface Seep

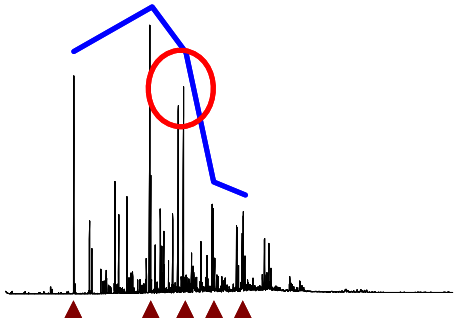




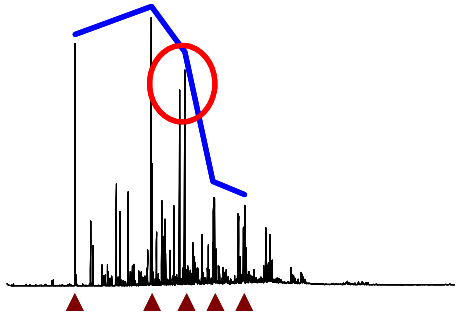
FS-Halleck St Row-2 Surface Seep



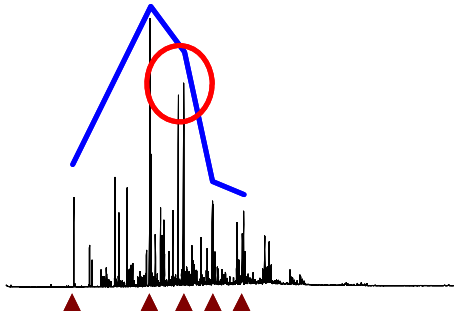
FS-Court St Row-1 Surface Seep



FS-RED HOOK-2 Surface Seep



FS-RED HOOK-4 Surface Seep



Selected PAHs (▲)
N0 Naphthanlene
P0 Phenanthrene
PY0 Pyrene
C0 Chrysene
BAP Benzo(a)pyrene

Color Key
- Petroleum
- Tar and Soot
- QC
- Other

Weathering
Light = N0
Moderate = P0
Heavy = PY0
Severe = BAP

Figure 3. Vertical Sediment Fingerprints from Selected Dated Cores (EPA 8270C GC/MS TIC).

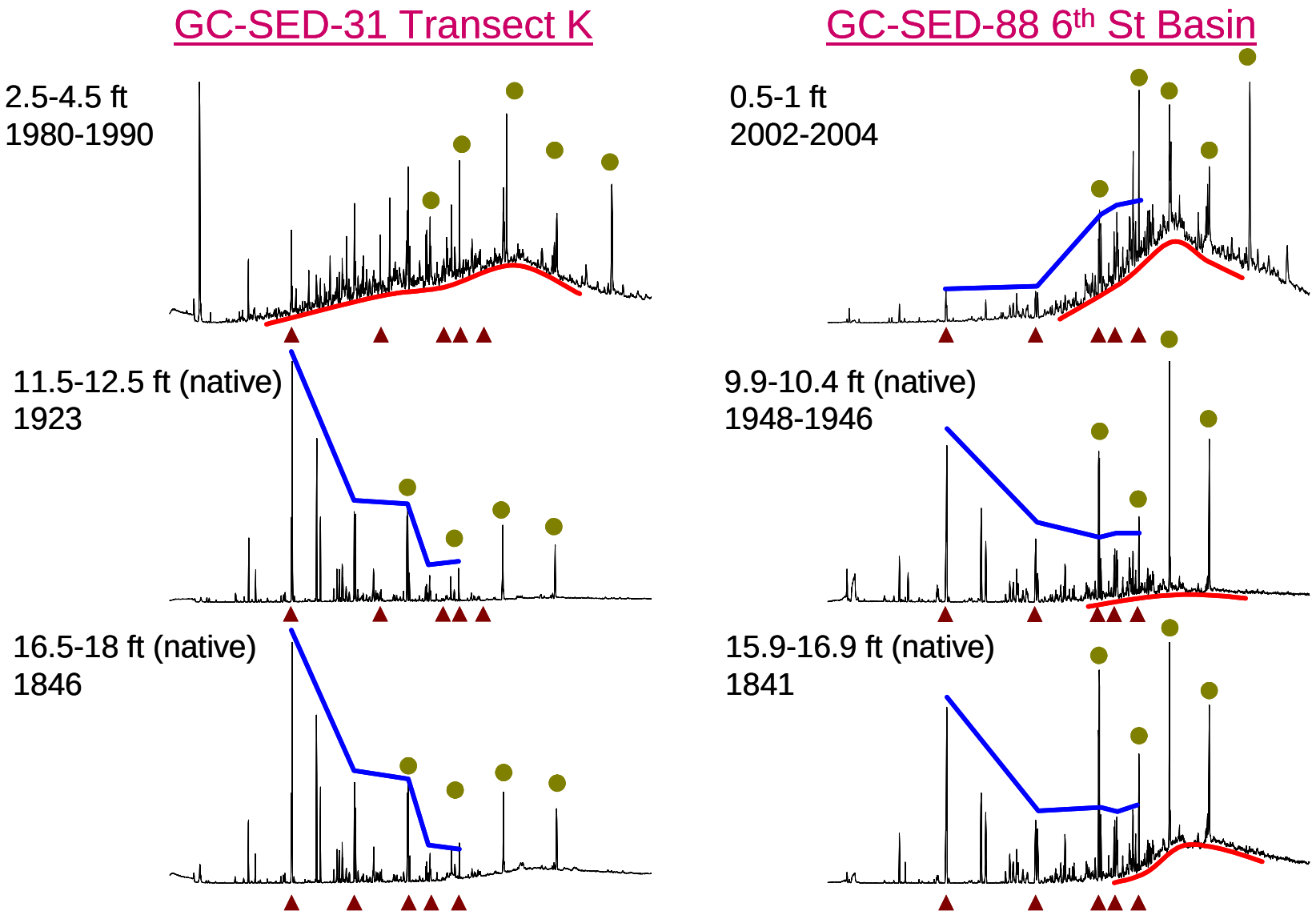


Figure 4a. Double PAH Ratio Plots Horizontal Sediment Grouping.

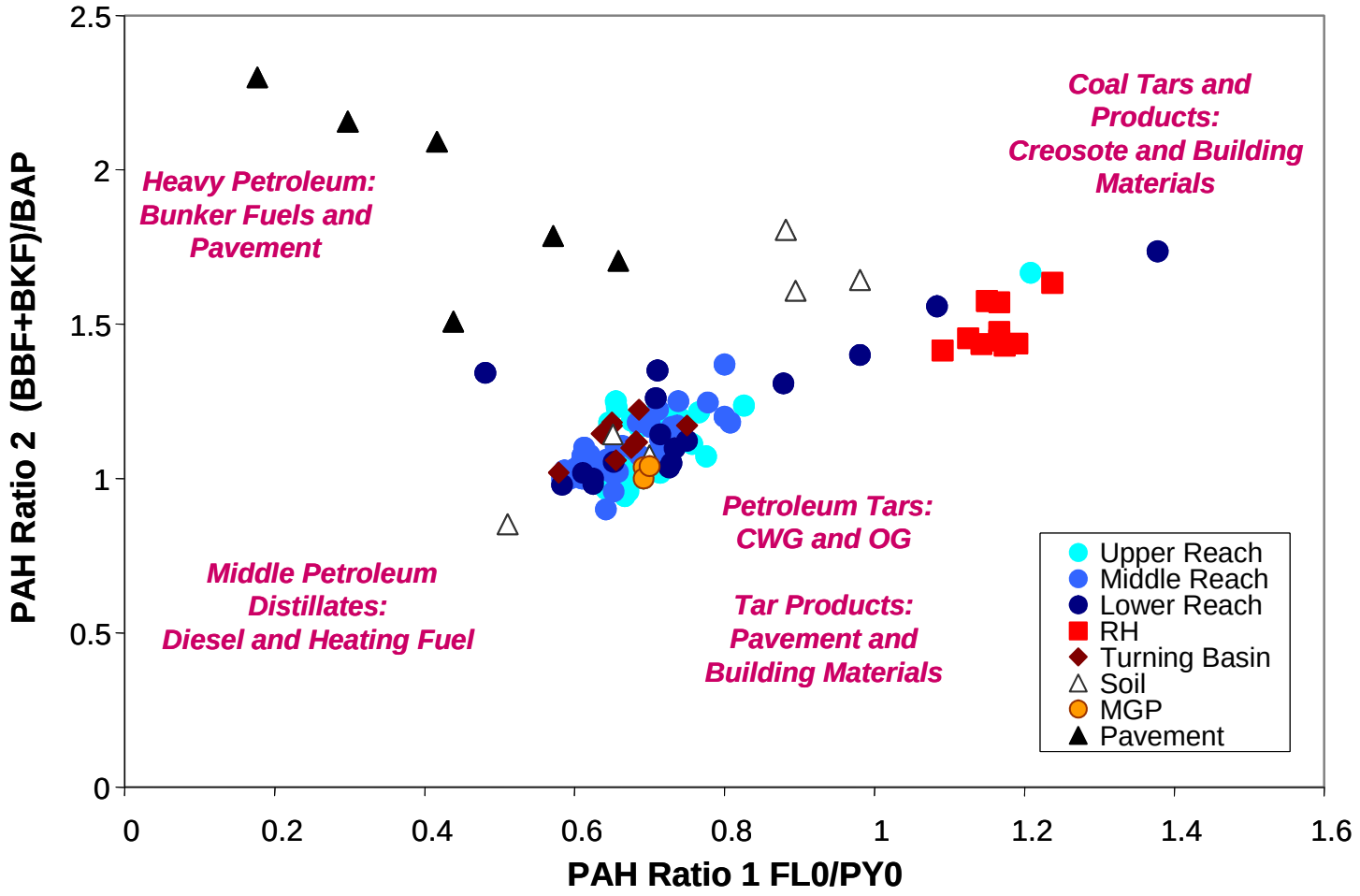


Figure 4b. Double PAH Ratio Plots Precision of Citizens Tar Signature.

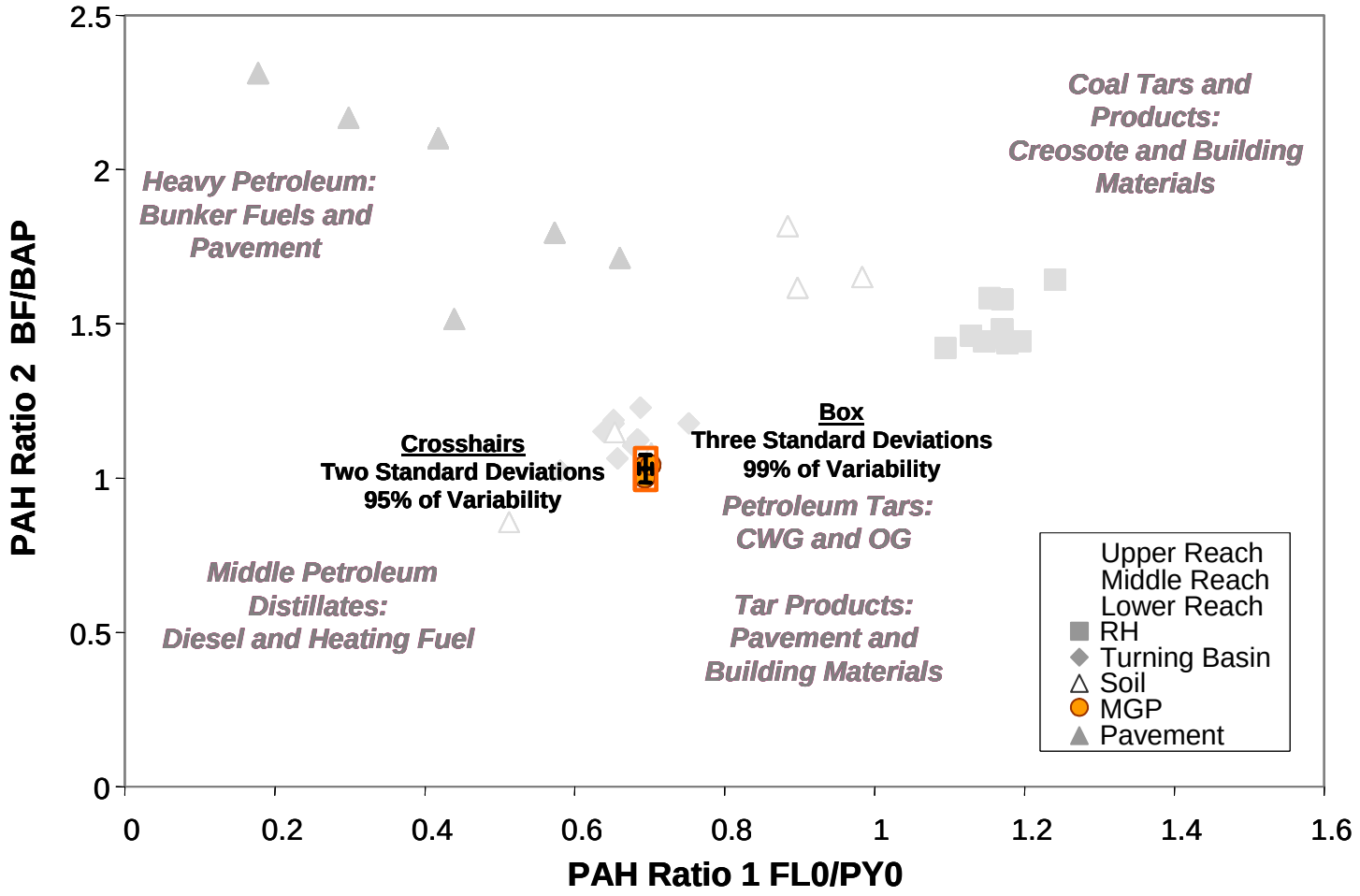


Figure 4c. Double PAH Ratio Plots Citizens Signature Among Sediment Reaches.

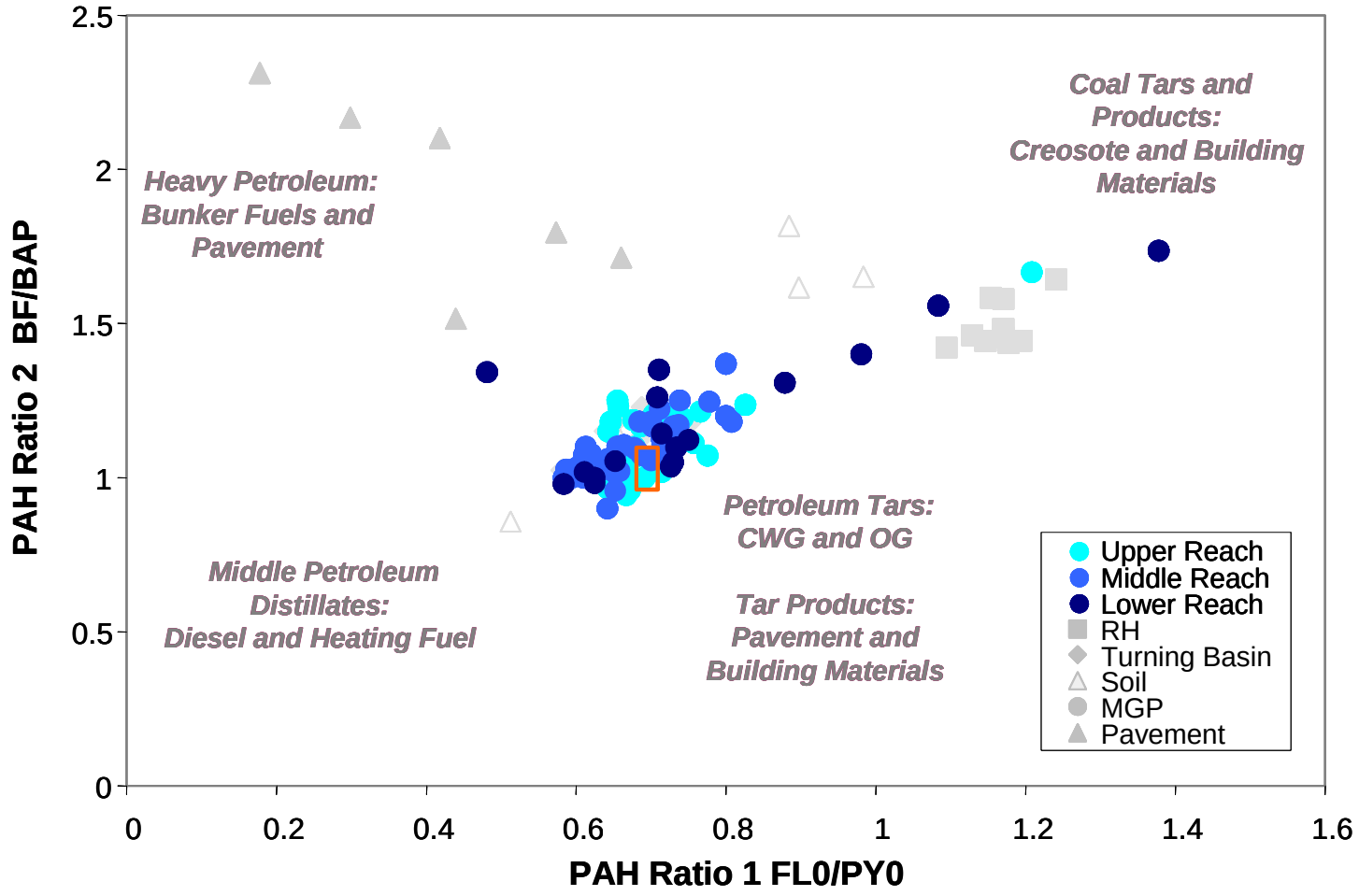


Figure 4d. Double PAH Ratio Plots Citizens Signature Among Native Sediments.

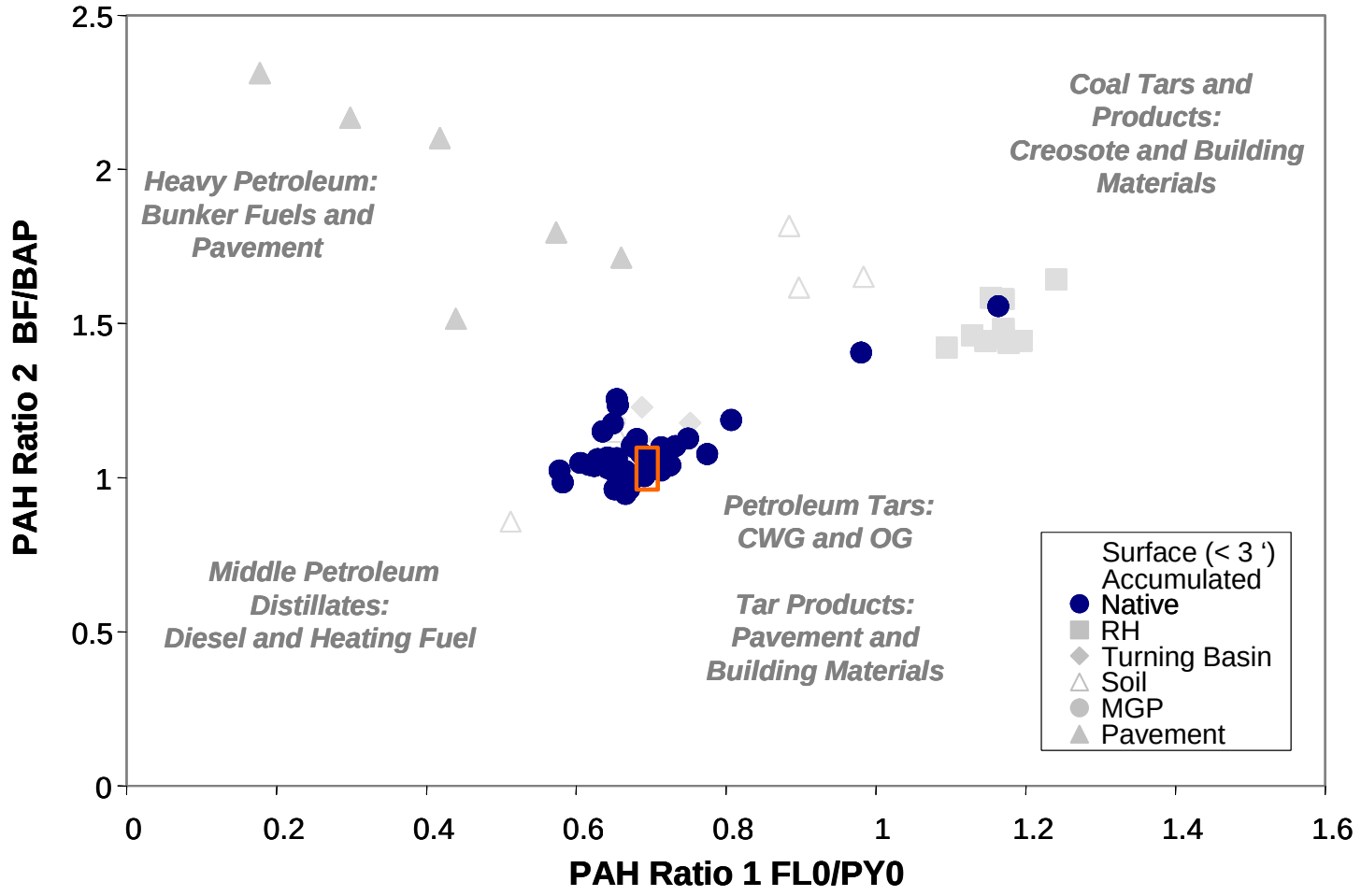


Figure 4e. Double PAH Ratio Plots Citizens Signature Among Accumulated Sediments.

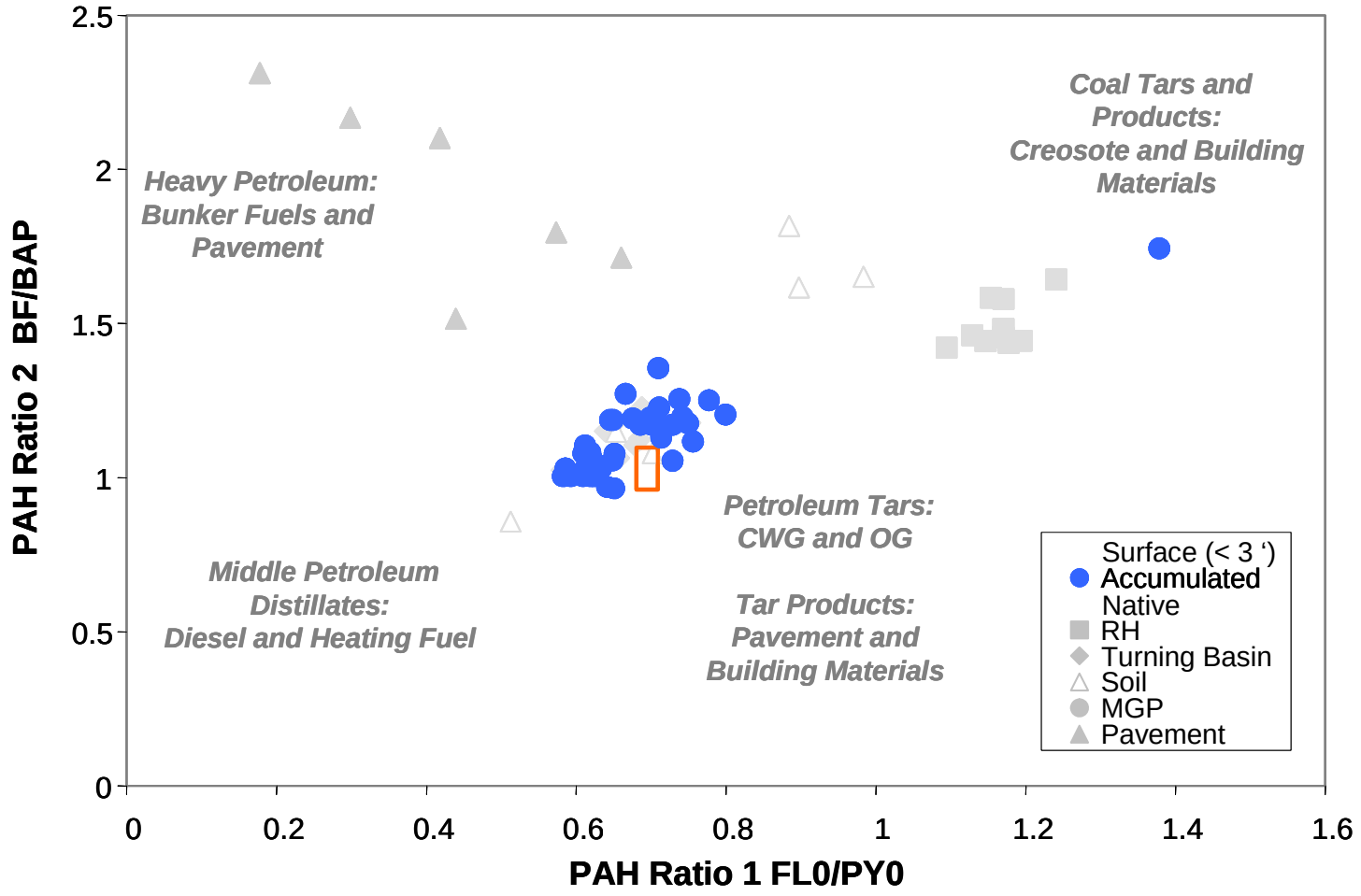


Figure 4f. **Double PAH Ratio Plots Citizens Signature Among Surface Sediments.**

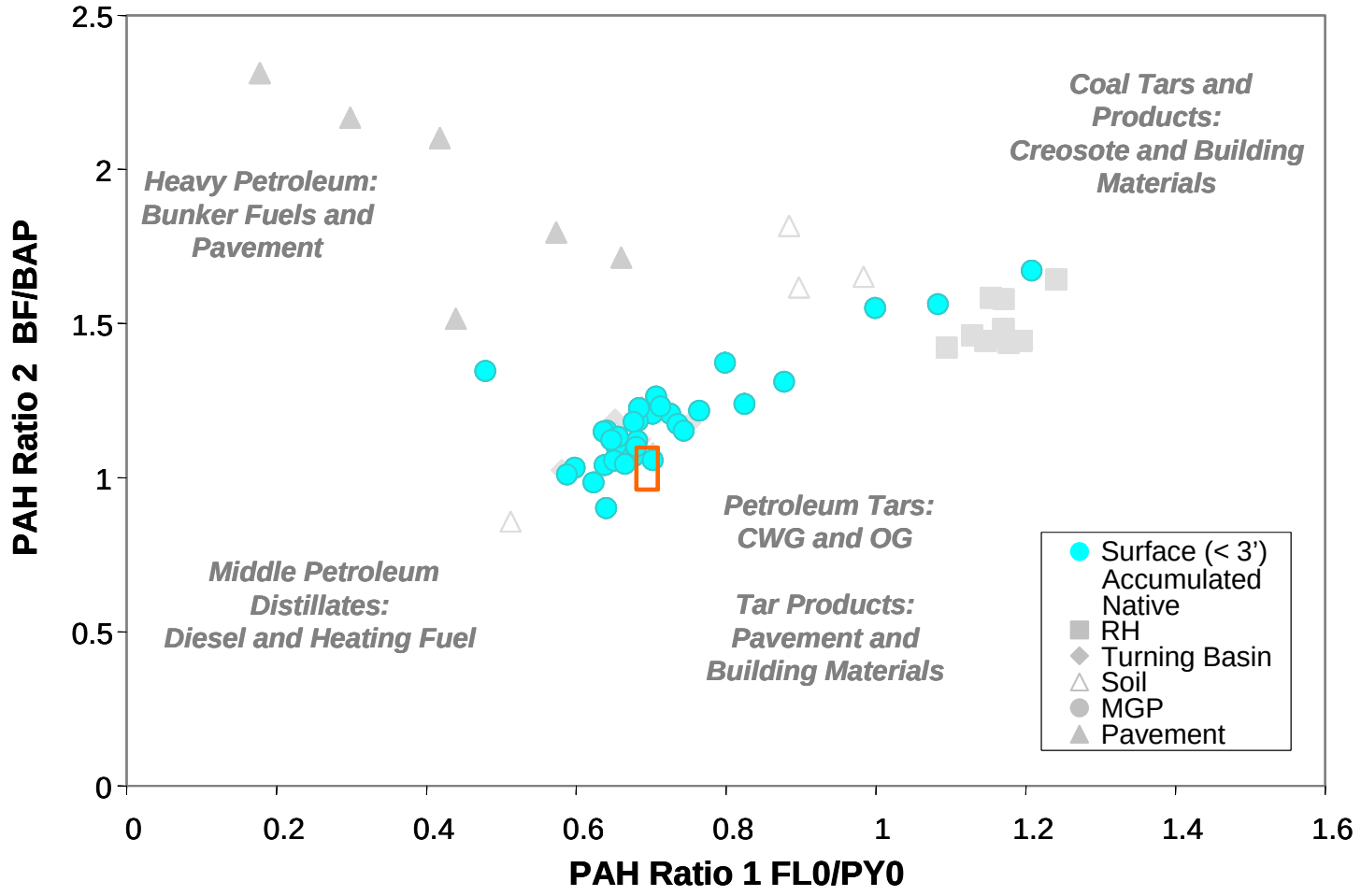


Figure 5. **Petroleum and Tar in Forensic Samples with Cores Normalized to the Native Sediment Depth.**

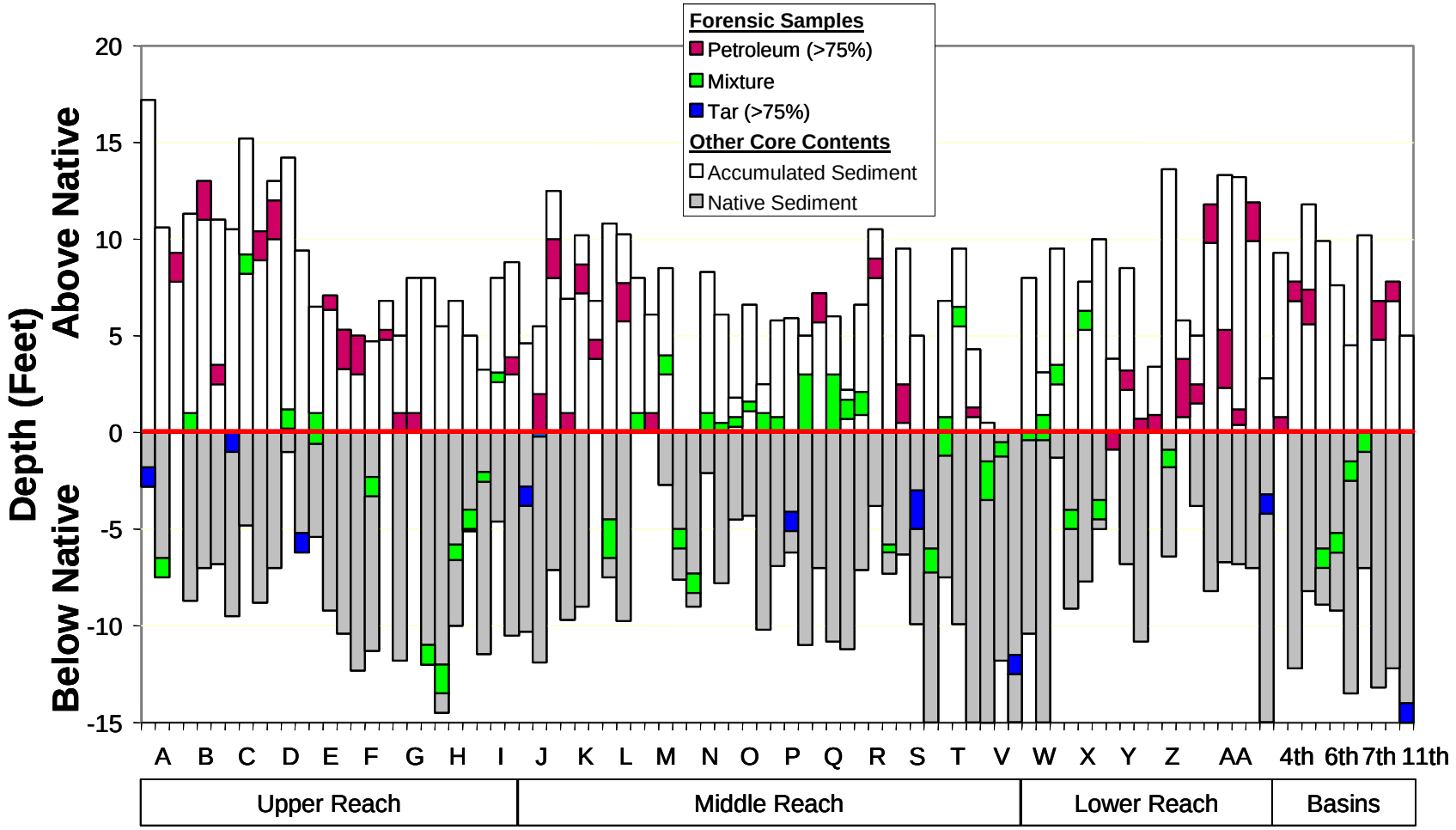
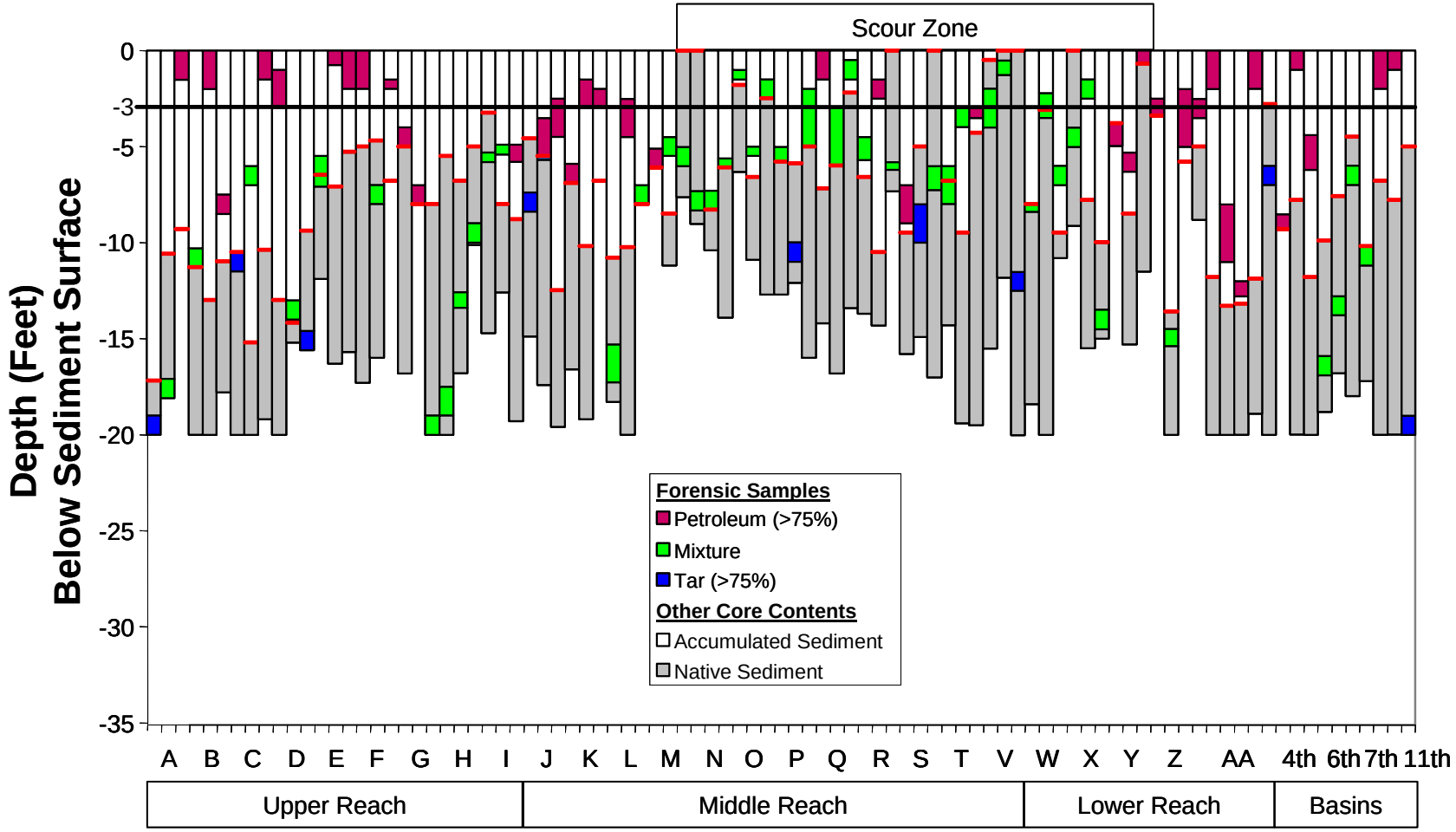


Figure 5. **Petroleum and Tar in Forensic Samples with Cores Normalized to the Bottom of the Canal.**



Attachment C
High Resolution Hydrocarbon Fingerprinting Results by GC/FID

Attachment D
PAH Results
by GC/MS/SIM

Attachment E
Saturated Hydrocarbon Fingerprints by GC/MS/SIM

Attachment F
Triterpane Biomarker Fingerprints by GC/MS/SIM

Attachment G
Forensic Chemistry Laboratory Reports

Attachment H
Radionuclide Laboratory Report